AL/EQ-TR-1994-0036
Vol V

CONTAMINANT REMOVAL FROM PLATING BATHS BENCH-SCALE EVALUATION OF ELECTROLESS NICKEL BATH REJUVENATION
VOLUME V

ARMSTRONG LABORATORY

Prakash T. Palepu, Han Wu, J. Kevin Rose,
Satya P. Chauhan

Battelle
505 King Avenue
Columbus. Ohio 43201-2693

ENVIRONICS DIRECTORATE
139 Barnes Drive, Suite 2
Tyndall AFB FL 32403-5323

March 1995

Final Technical Report for Period August 1992 - July 1993

Approved for public release; distribution unlimited.

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AIR FORCE MATERIEL COMMAND
TYNDALL AIR FORCE BASE, FLORIDA 32403-5323

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Ray A. Smith

RAY A SMITH, 1LT, USAF, BSC
Project Manager

Michael G. Katona

MICHAEL G. KATONA, PhD
Chief Scientist, Environics Directorate

Allan M. Weiner

ALLAN M. WEINER, LT COL, USAF
Chief, Environmental Compliance Division

Neil J. Lamb.

NEIL J. LAMB, Colonel, USAF, BSC
Director, Environics Directorate

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
3-15-95

3. REPORT TYPE AND DATES COVERED
Final Report 1 August 92 - 31 July 93

4. TITLE AND SUBTITLE
Contaminant Removal from Plating Baths; Volume V
Bench-Scale Evaluation of Electroless Nickel Bath Rejuvenation

5. FUNDING NUMBERS
F08635-90-C-0064

6. AUTHOR(S)
Prakash T. Palepu, Han Wu, J. Kevin Rose, and Satya P. Chauhan

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Battelle
505 King Avenue
Columbus Ohio 43201-2693

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Air Force
Armstrong Laboratory, AL/EQS
139 Barnes Drive, Suite 2
Tyndall AFB, Florida 32403-5323

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
AL/EQ-TR-1994-0036
Volume V

11. SUPPLEMENTARY NOTES
Contracting Officer's Technical Rep: Lt. Ray Smith
DSN 523-6462 or
(904) 283-6462

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for Public Release: Distribution Unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)
Electroless nickel (EN) plating is performed at all U.S. Air Force ALCs as part of depot level maintenance of aircraft parts. EN baths are frequently (once a month) dumped due to reaction byproduct (orthophosphite) build-up in the bath. Battelle was contracted by Armstrong Laboratory/Environics Directorate (AL/EQS) to identify, test, and implement a suitable technology to rejuvenate spent EN baths. After a technology review, three different technologies were considered for the rejuvenation of EN baths. After initial testing, one of them, the Stapleton Enfinity process, was selected for detailed bench scale testing. Plating tests with continuous bath rejuvenation were performed for 10 metal turnovers. Bath constituents were continuously monitored to determine the efficacy of orthophosphite (contaminant) removal from the bath. Plating quality, phosphorous content of deposit and deposit stress characteristics were analyzed and were found to meet the required specifications. Waste generated from the process (calcium orthophosphite filter cake) was collected and analyzed. The filter cake was successfully washed to reduce the nickel content to less than 5 ppm by TCLP. Alternate methods to monitor nickel content of the bath (in the presence of calcium) were developed. Plating rate, deposit characteristics, and waste generation were favorably compared to conventional EN processes. Based on results of these tests, it was recommend that a full-scale prototype unit of the Stapleton process with filter cake washing be designed, installed, and demonstrated at Tinker AFB OC-ALC.

14. SUBJECT TERMS
Electroless nickel plating, bath rejuvenation, orthophosphite removal from plating baths.

15. NUMBER OF PAGES
74

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

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PREFACE

This Final report represents the results of work done by Battelle in Columbus, Ohio and at Tinker Air Force Base, Oklahoma, on Volume V, "Electroless Nickel Bath Rejuvenation Prototype Demonstration", Contract No. F08635-90-C-0064, with the Environics Directorate, Armstrong Laboratory, Tyndall AFB, Florida.

This Interim Report, covers the period of performance from 1 July 1993 to 30th April, 1995. Our team's efforts were expanded by the conscientious involvement of others. We would like to express our appreciation to Glenn Graham, Patti Shreve, Jerry Jones, Dan Summrall, and Ernie Barlor of the U.S. Air Force, at Tinker Air Force Base for lending their time and their process experience. Their efforts and help were especially appreciated during the phase of prototype demonstration at the Tinker Air Force Base plating shop.

EXECUTIVE SUMMARY

A. OBJECTIVE

This report provides the details of the prototype installation and demonstration of the Stapleton electroless nickel bath rejuvenation system at the OC-ALC plating shop. The information in this report can be used by all USAF-Air Logistics Plating Shop personnel performing electroless nickel plating on aircraft parts.

B. BACKGROUND

Electroless Nickel (EN) plating is routinely performed at USAF-ALCs as a means of providing corrosion resistance to aircraft parts. EN plating is an autocatalytic chemical reaction with reaction byproducts accumulating in the bath. With usage, the byproducts accumulation slows the plating rate and renders the bath inoperable. Traditionally, EN baths are dumped once a month, constituting a significant hazardous waste source from plating shops. Battelle tested and evaluated several bath rejuvenation (byproduct removal) technologies and selected Stapleton Enfinity process for prototype installation at Tinker AFB. The process selectively removes the bath reaction byproduct by selective precipitation using lime and eliminates the need for bath dumps. The only waste from this process is a nonhazardous calcium orthophosphite sludge.

C. SCOPE

This report describes electroless nickel plating operations at ALCs and the need for bath rejuvenation. It describes the details of Stapleton EN bath rejuvenation prototype unit installation and demonstration at OC-ALC. Section I is an introduction to conventional EN processes and the problems associated with EN bath dumps. It also describes the prior work including the basis for technology selection and economic analysis. Section II briefly describes EN plating chemistry, current EN operations at ALCs and Stapleton bath rejuvenation technology. In Section III, the prototype equipment is described and operating procedures are provided. Section IV provides the details of EN plating and bath rejuvenation using the Stapleton unit at OC-ALC. Section V discusses the results of the prototype demonstration such as bath ion concentrations, plating rate and plating quality. Section VI provides the conclusions and recommendations.

D. CONCLUSIONS

During the prototype demonstration, EN plating equivalent to 10.0 bath metal turnovers (MTOs) was accomplished while maintaining the bath contaminant at 2.0 MTOs equivalent. Bath rejuvenation unit was very effective in removing the primary bath contaminant (orthophosphite ion). Nickel utilization was 98.1 percent compared to 75 percent in conventional EN processes. This translates to a reduction of 93 percent in discharge of nickel from EN plating. Although there were some mechanical malfunctions (at around 6.3 MTOs of operation) during the demonstration, the equipment was repaired and plating continued until 10 MTOs were achieved. Overall, the system performance and plating rate and plating quality were as expected and consistent with earlier bench-scale results. It is concluded that Stapleton EN bath rejuvenation system is an effective and economically viable alternative to conventional EN plating and it eliminates the periodic bath dumps associated with conventional EN baths.

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SECTION I
INTRODUCTION

The five Air Force Air Logistic Centers (AF-ALCs) carry out plating operations as part of their weapon systems overhaul and maintenance operations. During plating, a variety of contaminants, specially ionic species, accumulate in the plating baths, interfere with the plating process, and degrade deposit characteristics. This leads to periodic dumping of the baths which constitute hazardous waste. To help alleviate this problem for the Air Force, the Environics Division of the Armstrong Laboratories contracted Battelle to carry out a research and development project, titled "Contaminant Removal from Plating Baths." The specific objective of this project was to develop separation technologies to remove contaminants from and thus rejuvenate two different nickel plating baths: electroless nickel (EN) and nickel- strike (Ni-Strike).

The results from this project are reported in six volumes as follows:

Volume I. Bench-Scale Evaluation of Electroless Nickel Bath Rejuvenation

Volume II. Bench-Scale Evaluation of Nickel-Strike Bath Rejuvenation

Volume III. Economics of a New Nickel-Strike Bath Rejuvenation Process

Volume IV. Economics of a New Electroless Nickel Bath Rejuvenation Process

Volume V. Electroless Nickel Bath Rejuvenation Prototype Demonstration

Volume VI. Nickel-Strike Bath Rejuvenation Pilot Plant Demonstration.

This volume (No. V) covers the demonstration of a prototype for electroless nickel bath rejuvenation.

A. OBJECTIVE

The objective of the work reported in this volume was to design, procure, install, and test a prototype for electroless nickel bath rejuvenation.

B. BACKGROUND

Electroless nickel plating is a process that is driven by a nonelectrolytic chemical reaction process that forms a uniform deposit on complex-shape parts. Because of the uniformity of the deposit and the excellent corrosion resistance of the deposit under severe environments, electroless nickel (EN) plating is commonly used in the aircraft industry. In particular, all five of the U.S. Air Force ALCs use electroless nickel plating as part of the depot level maintenance of aircraft. Since EN plating is based on a chemical reaction, the accumulation of reaction byproducts in the bath slows

down the bath performance and degrades the deposit characteristics. EN baths are dumped frequently (about once a month) and constitute a source of hazardous waste at ALC's plating shops. The complex chemistry of the EN baths makes their treatment at the on-site industrial waste treatment facility (IWTP) difficult. Hence, the search for technologies to rejuvenate spent electroless nickel baths so as to eliminate the frequent dumps was initiated under the Environics contract with Battelle.

Technology selection, development, and demonstration testing for the rejuvenation of EN baths was performed under four subtasks. The first subtask identified the problem, discussed the prior efforts by the industry and the U.S. Air Force to develop rejuvenation technologies, and identified potential technologies for bench-scale testing. In the second subtask, the potential technologies were tested. Specifically the testing was carried out in a 15-gallon bath at Battelle and coupons were plated as per Tinker AFB (OC-ALC) specifications. Three different technologies, membrane electrolysis with a ceramic membrane, electrodialysis and selective precipitation were tested in bench-scale apparatus. These bench-scale tests and results are described in Volume I report "Bench-Scale Evaluation of Electroless nickel Bath Rejuvenation." Based on these bench-scale tests, one particular technology, "Stapleton Enfinity Electroless Nickel Bath Rejuvenation System," a selective precipitation technique, was selected as a candidate for prototype installation and demonstration at Tinker AFB, Oklahoma. The Stapleton Process met the OC-ALC requirements on deposit quality (such as deposit stress, absence of pitting, and phosphorous content), plating rate and required deposit thickness of at least 25 mils. It continuously removed the bath contaminants (reaction byproducts) by selective precipitation, thus, preventing the bath from aging. The details of the Stapleton rejuvenation process are described in the next section.

After the bench-scale tests, an economic and feasibility analysis was performed on the Stapleton system as part of the third subtask. This analysis considered the operating conditions at a representative ALC (OC-ALC) with respect to plating load, amount of plating performed in a year, cost of bath make-up, manpower requirements, waste generation and disposal costs. Based on this analysis, it was concluded that Stapleton Rejuvenation System has an economic payback of 3 years and it was recommended for prototype design, procurement installation and demonstration at OC-ALC. The details of economic analysis are given in Volume IV, "Economics of a New Electroless Nickel Rejuvenation Process." The rest of this report describes the design, procurement, installation, and demonstration of Stapleton EN bath rejuvenation system at OC-ALC.

C. APPROACH

After the U.S. Air Force acceptance of the Stapleton rejuvenation system for installation and demonstration at OC-ALC, the following approach was used to implement the prototype demonstration. A specification bid was prepared in consultation with OC-ALC plating shop personnel whereby the system was sized and designed to meet the requirements of OC-ALC. After the unit's construction, preliminary acceptance tests were conducted by Battelle at the vendor site. The unit was shipped and installed at OC-ALC plating shop in cooperation with OC-ALC and Stapleton (vendor) with Battelle supervision. A test plan was prepared for the prototype demonstration of the rejuvenation system at OC-ALC. After the acceptance of the test plan by U.S. Air Force and OC-ALC personnel, Battelle conducted the testing in two parts. The initial bath rejuvenation testing was conducted over a 5-week demonstration campaign, spread over a 10-week period due to unavailability of parts to be plated, where EN plating was performed and the EN bath was continuously rejuvenated. After this testing, several modifications were made to the system to correct the problems encountered. Subsequently, a 2-week demonstration campaign was successfully carried out at OC-ALC. The subsequent sections of this report describe these efforts in detail and conclude with a discussion of the results and recommendations.

SECTION II
PROCESS DESCRIPTION

A. ELECTROLESS NICKEL PLATING

Electroless nickel plating, as the name implies, is a non-electrolytic process in which a nickel-phosphorous deposit is formed on an active surface by means of a chemical reaction*. Nickel ions (Ni^{2+}) and hypophosphite ions ($H_2PO_2^-$) react in an aqueous solution in an autocatalytic manner to form the nickel-phosphorous (Ni-P) deposit. In addition to these ions, the bath formulation contains chelating agents that act as bath stabilizers to prevent catastrophic deposition of nickel. The ionic reactions are:

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+ \quad (1a)$$

$$3H_2PO_2^- \rightarrow H_2PO_3^- + H_2O + 2OH^- + 2P \quad (1b)$$

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2 \quad (1c)$$

The overall reaction to achieve a nickel to phosphorous ratio of 10:1 by weight (5 to 1 molar ratio) is:

$$Ni^{2+} + 3.3\ H_2PO_2^- + 2.7\ H_2O \rightarrow Ni + 3.1\ H_2PO_3^- + 0.2\ P + 1.8\ H^+ + 2\ H_2 \quad (2)$$

As shown in Reaction (2), in addition to the Ni-P deposit, the reaction produces orthophosphite ($H_2PO_3^-$) as the primary reaction byproduct and also produces H^+ ions (which reduce the bath pH continuously) and evolves hydrogen. As the reaction proceeds, nickel and hypophosphite consumed by the reaction are replenished by chemical additions so as to maintain their concentrations at set levels. In conventional electroless nickel (EN) plating baths, the source of nickel is aqueous nickel sulfate and the source of hypophosphite is aqueous sodium hypophosphite. In these baths, sulfate and sodium do not participate in the reaction and they also accumulate in the bath. The age of EN baths is measured in metal turnovers (MTOs); 1 MTO is defined as the deposition of all the nickel originally in the bath. In conventional EN baths, as the bath ages, reaction byproduct orthophosphite

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* For additional details on electroless nickel process chemistry, see Volume I of this project report, published on August 12, 1993.

ion and also sodium and sulfate ions accumulate in the bath. Eventually this accumulation slows down the plating rate and more importantly changes the deposit characteristics; the deposit stress changes from compressive to tensile. Since this is unacceptable for aircraft parts, the bath is then discarded and a new bath is made-up. At Tinker AFB, conventional EN baths are dumped after 4 MTOs.

B. STAPLETON ELECTROLESS NICKEL BATH

Stapleton electroless nickel bath has modified chemistry. The source of nickel and hypophosphite in the bath make-up and replenishment is an aqueous solution of nickel hypophosphite. This implies that sodium and sulfate ions that accumulate in a conventional EN bath are not present in the Stapleton EN bath. Hence, the only accumulation in the bath is the orthophosphite ion as the reaction byproduct. Other aspects of EN plating with Stapleton chemistry is similar to conventional EN plating; consumed nickel and hypophosphite are replenished periodically (by adding nickel hypophosphite) to maintain the nickel concentration within a set range. Bath stabilizers are also added periodically. The phosphorous content of the Ni-P deposit is expected to be around 10 percent. Stapleton EN bath intrinsically plates faster the conventional EN baths.

C. PLATING BATH REJUVENATION

Stapleton EN bath, because of simpler chemistry, has the unique advantage of bath rejuvenation. Since the baths' only byproduct is orthophosphite ion, if it can be removed periodically from the bath, the bath never ages and plating rate and deposit characteristics do not change with time; i.e., the bath need not be discarded like conventional EN baths. This orthophosphite removal is accomplished by the bath rejuvenation unit. It essentially treats a slip stream from the bath with calcium hydroxide [$Ca(OH)_2$]. The calcium hydroxide reacts with the orthophosphite in the bath to form insoluble calcium orthophosphite as per the reaction.

$$Ca(OH)_2 + H_2PO_3^- \rightarrow CaHPO_3 + H_2O + OH^- \tag{3}$$

The precipitated calcium orthophosphite [$Ca(OH)_2$] is filtered and removed. The filtrate containing the nickel and hypophosphite values is returned to the bath.

The amount of $Ca(OH)_2$ added should be sufficient to stoichiometrically react with most of the orthophosphite in the batch being treated for; e.g., a 150-gallon bath of Stapleton EN bath at 2 MTOs

orthophosphite level has 60 grams/L of orthophosphite ion and 6.9 pounds of $Ca(OH)_2$ are required to precipitate all the orthophosphite as $CaHPO_3$. Ideally, 6.5 pounds of $Ca(OH)_2$ are added to treat the 15-gallons of EN bath at an orthophosphite level of 2 MTOs. This would remove most of the orthophosphite and still maintain a stoichiometric excess of orthophosphite to $Ca(OH)_2$ ratio and prevent any unreacted $Ca(OH)_2$ in the slurry. The reaction is pH sensitive and $CaHPO_3$ formation is best in the pH range of 8.25 to 8.75. The formation of OH^- ions in the precipitation reaction is sufficient to raise the pH of the slurry from 4.8 (bath pH) to the desired pH of 8.25 to 8.75. The increase in pH has an additional benefit; the filtrate returning to the bath is at high pH relative to the bath and balances out the H^+ ions being produced in the bath from the EN reaction [Equation (2)]. This in effect reduces or eliminates the addition of ammonia to the bath in order to maintain the bath pH within a set range (4.7 to 5.0). For operational convenience, it is preferable to treat a fixed amount of the bath (e.g., 15-gallons) and to add a fixed amount of $Ca(OH)_2$ (e.g., 6.5 pounds) to the batch. During the orthophosphite precipitation reaction, some calcium ions go into solution and are introduced into the bath when the filtrate is returned to the bath. The amount of calcium entering the bath is determined by the solubility limit of calcium at the filtrate pH and eventually the calcium content of the bath reaches a steady state value of around 800 to 1200 ppm. This level of calcium in the bath remains in solution and laboratory tests have shown that it does not affect the plating quality.

The removal of orthophosphite in the bath as calcium orthophosphite filter cake by the bath rejuvenation unit removes the only bath contaminant and maintains the bath at a low orthophosphite level. Ideally, the bath is maintained at orthophosphite level in the range of 2 to 3 MTOs by periodic bath rejuvenation. Hence, the bath continues to plate similar to a new conventional EN bath even though its age based on nickel replenishment is many tens of MTOs.

SECTION III
PROTOTYPE EQUIPMENT DESCRIPTION

A. PROCESS AND EQUIPMENT SPECIFICATION

Based on the results of the bench-scale experiments on the rejuvenation of electroless nickel baths at Battelle, the Stapleton Enfinity (Stapleton) process was selected and recommended for full-scale demonstration at OC-ALC (Tinker AFB). After the acceptance of the recommendation by the U.S. Air Force, Battelle prepared a "Specification for Bid" in consultation with the Process Engineering and Plating Shop personnel at Tinker AFB (see Appendix A). The bid specification sized the system, specified the equipment details and performance criteria so as to meet the needs of Tinker AFB's electroless nickel plating needs. These included the bath size (150-gallons), expected plating rate, deposit thickness, minimum phosphorous content of the deposit, expected metal turnover rate and rejuvenation frequency. The vendor (Stapleton Technologies, Long Beach, California) was then given the specifications and cost and delivery schedules were discussed and accepted. After the unit was fabricated, Battelle personnel conducted preliminary acceptance tests at the vendor site using EN plating solutions from a local plating shop. The unit was then accepted with minor modifications and then shipped to Tinker AFB for installation.

B. EQUIPMENT DESCRIPTION

A photograph of the "Enfinity PU-2 Unit" is shown in Figure 1 and a process schematic is shown in Figure 2. The unit is skid-mounted, has a footprint of 86" x 44" x 84" high and weighs approximately 900 pounds. In addition, the process requires a box or drum for the filter cake to be dumped into. The process unit is comprised of pneumatically driven pumps, a S.S. water-cooled reactor tank w/mixer, level sensors, and temperature sensors, a pneumatically driven vacuum pump, filter, filtrate recovery tank, pH meter and is controlled by a computer enclosed in a NEMA 4 control panel. All valves are either electrical solenoids or pneumatically operated. Utilities required for the process are 110 VAC electrical, 85 psi clean air supply, 20 psi deionized water and 40 psi cooling water. The cooling water is for cooling of the reactor and is once-through and, therefore, is drained to a sewer.

The reactor is constructed of 316 low carbon stainless steel, is 30-gallons in volume, and surrounded with a cooling water jacket. The reactor is fitted with an air driven agitator, high and low

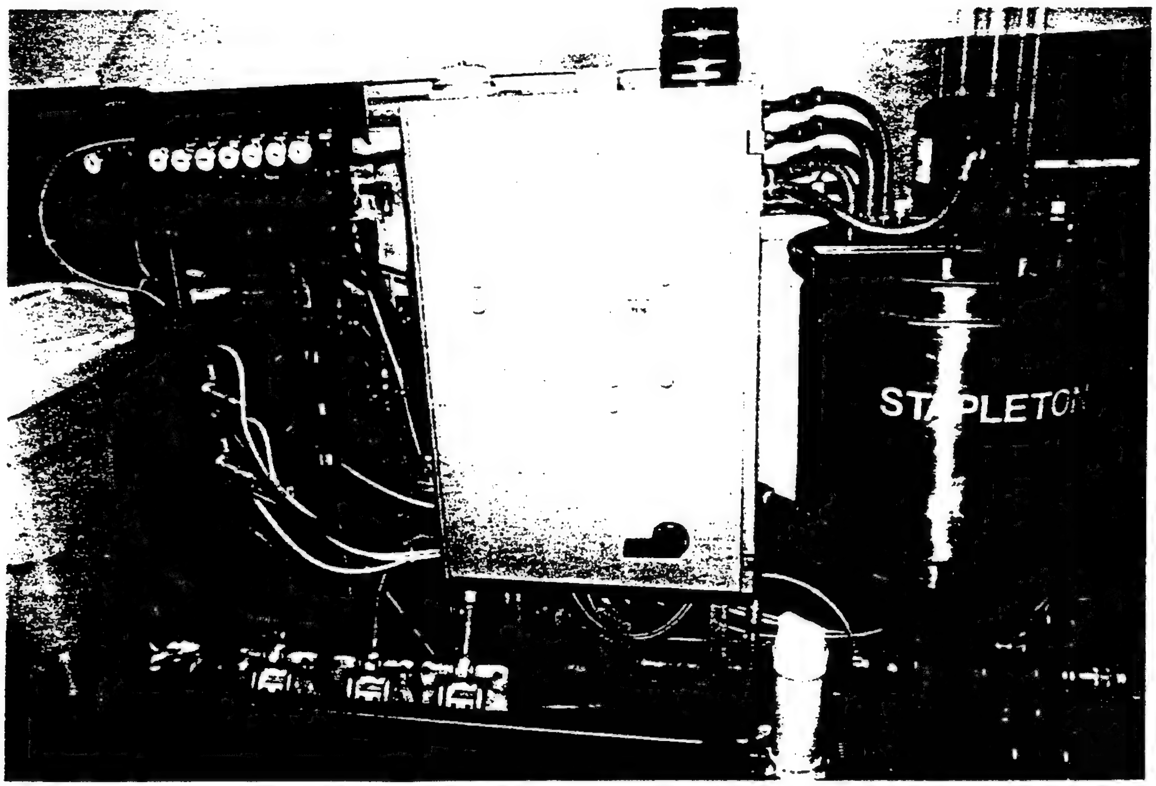

Figure 1. Prototype of the Stapleton Electroless Nickel Bath Rejuvenation System.

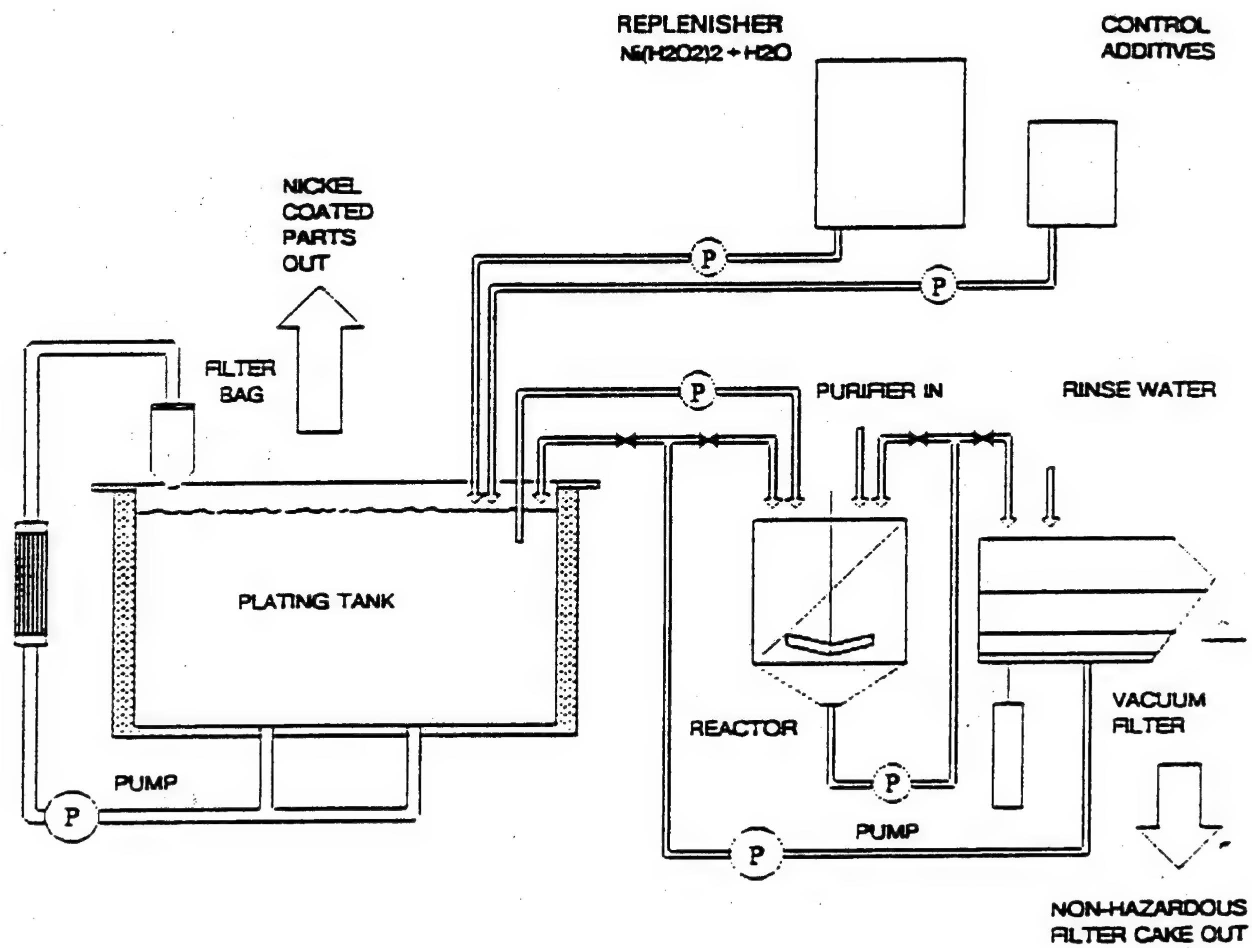

Figure 2. Schematic of the Stapleton Enfinity PU-2 Unit.

level probes, a pH probe and a temperature sensor. All of the piping, pumps and valves on the unit that contact the plating solution are of stainless steel, CPVC, Poly-propylene or Kynar.

The skid, framework, and filter housing are constructed of carbon steel and painted with epoxy paint. All pumps are air-operated diaphragm type pumps. The electrical fixtures, controls, solenoids and enclosures are of NEMA-4 construction. The connections of the "Enfinity" PU-2 unit to the EN plating bath is provided by polypropylene tubing and CPVC pipe which allow for the transfer of plating solution to the reactor, the return of purified filtrate to the bath and the addition of the required bath replenisher chemicals.

The operation of the PU-2 full-scale prototype unit is semi-automatic; i.e., the operator is required to push buttons to initiate the various processing steps after ascertaining the need for such by analysis of the plating bath solution.

At the request of Tinker AFB, cake washing beyond the on-filter washing was not incorporated in the system. It was recommended that an additional cake washing system be added in the future, only if necessary.

C. OPERATING PROCEDURE

As mentioned in the "Process Description" section, the Stapleton Process removes the primary bath contaminant, the orthophosphite byproduct by reacting it with hydrated lime [$Ca(OH)_2$] and precipitating it as calcium orthophosphite. The bath is started and the bath orthophosphite level is allowed to accumulate in the bath until the level reaches at least two metal turnovers (MTOs). The bath rejuvenation is then started. Rejuvenation consists of removal of 10 percent of the bath (15-gallons), treatment with calcium hydroxide, filtration and filtrate return. Rejuvenation frequency and time are determined by the plating rate; i.e., if the bath loading and plating rate are such that it requires 40 hours to plate 1 MTO, then the bath rejuvenation is performed approximately once every 8 hours. Bath replenishment of adding nickel and hypophosphite is performed similar to a traditional bath; i.e., nickel concentration level is maintained between 95 percent to 100 percent of full strength.

Once the plating bath has plated two metal turnovers (MTO) equivalent, rejuvenation can be initiated. Prior to starting rejuvenation, 15-gallons of bath make-up (7.5-gallons of HXIA and 7.5-gallons of water) need to be added to the filtrate holding tank. Rejuvenation is started by pressing the ADD button on the control panel. The PU-2 then pumps 15-gallons of bath solution from the plating tank to the SS reactor and the 15-gallons of bath make-up in the filtrate holding tank are pumped back

to the plating bath. At the same time the unit adds replenishment chemicals (HXIR and HXIC) equivalent to 3 percent of the bath volume. As soon as the 15-gallons of bath solution is in the rejuvenation reactor the agitator is started and cooling water flow through the cooling jacket is started to cool the solution to 100 F. When the solution has been cooled ($\approx$ 10 minutes), a READY light on the control panel lights indicating the unit is ready to treat the solution.

After adding a premeasured (6.5 pounds) of purifier (calcium hydroxide) to the reactor the TREAT button is pressed and digestion of the purifier and precipitation of orthophosphite as calcium orthophosphite is carried out. After 4 minutes of digestion, the slurry is pumped from the reactor to the filter and the vacuum filter pump is activated. Within 10 minutes the reactor tank is emptied of slurry as filtration continues. After completion of filtration as indicated by the level of vacuum maintained, a water spray rinse of the filter cake is initiated. Upon completion of filtration and rinsing, the UNLOAD light on the panel illuminates. Pushing the UNLOAD button allows the filter to lift and dump the cake into the collection bin. Pressing the RETURN button then returns the filter to its original position and rejuvenation is complete and the PU-2 is ready to accomplish another cycle.

A complete description of the PU-2 rejuvenation unit operating and maintenance procedures are given in the vendors "PU-2 Operating and Service Manual." Copies of this manual have been given to the Tinker AFB plating shop supervisors and operators. A short version of this manual is enclosed as Appendix B.

SECTION IV

PROTOTYPE DEMONSTRATION OPERATION AT TINKER AFB

A. INSTALLATION AND OPERATOR TRAINING

The PU-2 full-scale prototype "Enfinity" system was installed in the plating shop (Bldg 3001) at Tinker Air Force Base. The rejuvenation system was interconnected with two (2) 150-gallon electroless nickel plating tanks which previously employed the "Enthone" electroless nickel plating solutions. A test plan was prepared by Battelle for prototype demonstration and accepted by the U.S. Air Force. The test plan is given in Appendix C.

At Tinker the electroless nickel plating load is quite sporadic and not continuous (at a given deposit thickness) such as would be expected at a production/commercial plating facility. The EN plating requirements at Tinker typically vary from 10 to 25 mils thick on various shaped parts. The parts plated in the EN baths at Tinker AFB are bleed valves, sealing tubes, housing valves, bodyhousing air valves and air seals from the TF-33 engines on the KC-135 planes. All these parts require "build-up" of 10 to 25 mils of plating thickness.

After installation of the unit was completed the unit was leveled and the rejuvenation system was checked out mechanically using hot water. Any minor piping leaks caused by shipping were repaired and the system control logic was verified and adjusted for the expected plating load.

The 150-gallon plating tank was made-up with Stapleton electroless nickel chemicals and water in the desired ratio and plating was started on Tinker parts known as flash parts; i.e., requiring only 1 to 2 mil coating. Also, during this initial period of plating, training was provided to the Tinker operators by both Stapleton and Battelle personnel.

B. BATH STARTUP

During a 2-week period of plating in November and December 1994, the bath had reached the 2.5 MTO level and was ready to start rejuvenation using the PU-2 system. During these initial periods of operation the PU-2 was used to make the required chemical additions to the plating bath. By pressing the ADD button on the PU-2 control panel the HXIR (replenisher), HXIC (control) and ammonia chemicals were automatically pumped into the bath in predetermined amounts to maintain the bath at proper nickel level and pH. During the 2.5 MTOs of plating, especially during the first MTO, the plating rate was substantially lower than expected. Initially, the problem was an imbalance

in the ratio of bath replenisher (nickel hypophosphite) to bath control (stabilizers and chelating agents). There was an excess of bath stabilizers because of replenisher line fouling. This caused the plating rate to be decreased. After this was corrected, plating rate increased but was still at about 70 percent of the expected plating rate of 0.35 mils/hour. This problem was traced to an imbalance in the bath control formulation, which had excess stabilizers to bath accelerators for the type of plating at Tinker (no dragout). This imbalance was corrected after about 2 MTOs of plating, and the rate increased substantially to about 95 percent of the expected plating rate during the last 0.5 MTO of plating. At this time, the plating bath was shut down due to the lack of parts to be plated at Tinker. Two of the four EN plating operators were trained in maintenance of the bath and the concept of the PU-2 rejuvenation system.

C. INITIAL BATH REJUVENATION TESTING

In January, 1995, the EN plating was restarted, the PU-2 rejuvenation system was operated for a period of about 2 weeks which brought total bath operation to over 6 MTO equivalent operation. Additional Tinker operator training was conducted during this period of operation.

During this period of operation, a total of 18 treatment (separation) cycles were completed with the PU-2. This allowed the plating bath to be maintained at a level of 2-3 MTOs. Samples of the filter cake, filtrate, and plating solution were obtained for analyses. The analytical and operating results obtained are discussed in the following sections of this report.

Also during this period of operation of the PU-2 Lieutenant Smith of Tyndall Air Force Base visited Tinker to observe operations and Battelle videotaped the operation and visit.

D. MECHANICAL MODIFICATIONS TO THE PU-2 UNIT DURING INITIAL REJUVENATION TESTING

Some problems were encountered during the initial operation of the unit. The problems encountered were both mechanical and technical in nature. However, most of the problems encountered were of the type typical to the start-up of a new process and were overcome during this operating period. The technical problems encountered are discussed in the following sections of the report. Following is a discussion of the mechanical problems encountered and solved during start-up.

Several small leaks in the plumbing of the PU-2 were found and repaired. These leaks were primarily due to fittings loosening or breaking during shipment of the unit from the vendor to Tinker. Another mechanical type problem was failure of the liquid level control in the reactor tank. The level

control probe used was of the RF type and is believed to be interfered with by the hot, humid conditions in the reactor during digestion and precipitation. Initially (between 3 and 6 MTOs), the problem was overcome by disconnecting the level sensor and allowing the pump to be stopped by a timer in the control logic which is the fail-safe mode of operation in the case of probe failure. Later at 6 MTOs of operation, the RF type level sensor/switch was replaced by a mercury tilt float switch which performed flawlessly for the remainder of plating (> 10 MTOs).

Another mechanical type problem encountered is inadequacy of the filter cake water spray rinse. Part of this problem may be due to the low pressure (due to pump shut-off) in the demineralized water line at Tinker. That is, there are times, particularly on the night shift, that this water pressure is well below the 30 psi required for adequate spray nozzle operation. In addition, tests during the prototype demonstration showed that best filter caking washing is achieved when the cake is deluged or flooded with water. Hence, the rinse water timer changed in the control logic from 3 minutes to 1 minute and additional spray nozzles were installed (at 6 MTOs) so that all the rinse water is added essentially all at once to effect better cake washing. Continued operation of the unit did indeed show better washing results.

Probably the major problem encountered during the PU-2 operation was the development of a leak around the filter cloth which allowed a portion of the filter particles (calcium orthophosphite) to be pumped back to the plating bath. These particles in the bath could have caused a disastrous plate out of nickel in the bath but was avoided since as the calcium particles were plated with nickel they became heavy enough to sink to the bottom of the bath. This plate out and particles in the bath problem will be discussed further in the following section. The filter leak was due to incorrect installation and securing of filter cloth to the filter housing by the vendor. The problem was corrected by caulking the area of leak with silicon bath tub caulk. In addition, it was noticed that during the initial stages of filtration, some fines were passing through the filter since sufficient layer of cake had not yet been formed on the filter (dynamic filtration). Hence, the initial recycle time of the filtrate back to the filter was increased from 1.5 minutes to 3 minutes.

Other modifications to the PU-2 Unit included (a) replacing the agitator mounting bracket with a sturdier bracket, (b) replacing the filtrate line to the filtrate holding tank with closed loop piping to prevent particulate overflow into the holding tank in the case of future mishaps, (c) increasing the digestion time in the reactor from 4 minutes to 6 minutes to form bigger crystals and (d) allowing the bath orthophosphite level to be closer to 3 MTOs equivalent than 2 MTOs so that the

addition of 6.5 pounds of lime to a 15-gallon batch maintains a stoichiometrically excess quantity of orthophosphite, thus, minimizing the existence of unreacted lime fines in the filtrate slurry.

Overall operation of the PU-2, being a new technology, was for the most part satisfactory although some of the problems encountered were quite bothersome and may have given the impression of requiring a great amount of operator attention to OC-ALC production personnel. However, most of the problems were of the type normally encountered with start-up of a new process system and they were overcome. The list of mechanical modifications that were made at 6 MTOs of operation, are listed in Table 1. These modifications were made to the PU-2 Unit at around 6 MTOs, when the filter developed a leak. During the time of mechanical modifications, the plating bath was stored in 55-gallon drums.

E. ADDITIONAL TESTING OF BATH PLATING AND REJUVENATION

After the completion of the mechanical modifications to the PU-2 Unit, the bath solution stored in drums was transferred back to the plating tank in March, 1995, and plating and rejuvenation was restarted. Initially, plating was performed with test coupons (6" x 6" mild steel and stainless steel) to monitor the equipment performance. After satisfactory performance real parts (body valves and air seals from the TF-33 engine) were introduced along with the test coupons. Test coupons were removed from the bath sequentially at 10, 20, 30, 40, and 50 mil thickness of plating to monitor the plating quality. Plating continued for 2 weeks to ensure trouble-free operation of the bath and the rejuvenation system. At the end of 2 weeks, the bath age was past 10 MTOs, or 2.5 times the age of a spent conventional bath. The bath orthophosphite level was maintained between 2 and 3 MTOs equivalent. The plating was then voluntarily stopped and prototype demonstration was concluded. During the additional testing, the bath performance, plating rate, rejuvenation system performance were better than acceptable. The testing was thus concluded successfully.

TABLE 1. MECHANICAL MODIFICATIONS MADE TO THE PU-2 UNIT DURING PROTOTYPE DEMONSTRATION.

Item	Modification	Reason	Observed or Expected Improvement
Reactor Level Sensor	Replaced with mercury switch.	Irregular Sensing.	Consistent 15-gallon removal.
Filtrate Tank Bag Filter	Replaced with larger monofilament bag.	Bag plugging even with small amounts (100 g) of cake.	Prevent calcium entry into bath in the event of future mishaps.
	Replaced with closed loop piping.	Presently filtrate overflows when bag is plugged.	Prevents filtrate overflow in the event of bag plugging.
Agitator and Mounting Assembly	Replaced with sturdier mounting bracket.	Vibration in the present set-up.	Trouble free operation.
Rinse System	Modified to dump the rinse water quickly onto the cake.	Spray nozzle too slow. Corners of filter not rinsed properly.	Even lower levels of nickel in the cake due to proper rinsing.
Replenisher Drums	Shipped in heated trucks.	Solids settling during transportation through cold climates.	No feed line blockage. Better use of chemicals.
Digestion Time in Reactor	Increased from 4 min. to 6 min.	Small crystal size and long filtration time.	Elimination of fines in slurry and improved filtration time.
Time of Filtrate Recycle Back to Reactor	Increased from 1.5 min. to 3 min.	Possible pass through of fines during the initial stage of filtration.	Allows cake to form fully on the filter for better dynamic filtration and elimination of fines in the filtrate.
Purifier [$Ca(OH)_2$] Amount Added	Maintained excess ortho to purifier ratio.	Possible pass through of unreacted purifier fines into the filtrate.	Elimination of purifier fines in the filtrate.

SECTION V

PROTOTYPE DEMONSTRATION RESULTS AND DISCUSSION

The operational goals for the Stapleton PU-2 prototype demonstration at Tinker were to (1) plate up to at least six metal turnovers (MTOs), (2) attain a plating rate of 0.35 mils/hr, (3) maintain bath orthophosphite concentration between 2 and 3 MTOs equivalent by bath rejuvenation, (4) achieve good plating quantity with at least 10 percent phosphorous content in the deposit. Prototype demonstration commenced during the last week of November 1994, continued in the first week of December 1994. It was restarted and completed in the third and fourth weeks of January 1995 after 6 MTOs. At around 6 MTOs, plating was stopped to perform mechanical modifications to the PU-2 rejuvenation unit. After the completion of equipment modifications, plating was resumed in March, 1995, and it was continued for another 2 weeks until the bath age was past 10 MTOs. A total of 375 hours of plating was performed. During the demonstration, a plating log was maintained by the plating operators and Battelle personnel that recorded the bath conditions, bath additions and rejuvenations. The plating log is shown in Table 2. The results of the demonstration are described in this section and discussed relative to the operational goals.

A. BATH NICKEL CONCENTRATION AND pH

The desired nickel concentration in the bath is 6.6 grams/L. As the nickel concentration drops during plating, bath is replenished (by pushing on the ADD button on the PU-2) in 10 percent increments (0.6 gram/L) whenever the nickel concentration drops below 6.0 grams/L so the nickel concentration is maintained in the 6.0 to 6.6 grams/L range. Nickel measurements are made every 2 hours using a Hach colorimeter. The nickel concentration is shown in Table 2 as well as in Figure 3. As shown in Figure 3, the nickel concentration was maintained substantially in the 6.0 to 6.6 range during the entire demonstration period except during the sixth metal turnover. During that time the filter leak occurred, the bath was consuming nickel at an excessive rate due to the presence of calcium particles in the bath and the operators had difficulty in maintaining the nickel concentration in the 6.0 to 6.6 grams/L range. This is discussed later in the section on "Plating Quality."

Bath nickel measurement using the Hach colorimeter is new to EN plating at Tinker AFB. It was demonstrated by Battelle in laboratory testing phase (see Volume I of this Project Report) and is simpler and easier to use than the traditional EDTA titration. Comparison of colorimeter values with

TABLE 2. BATH CONCENTRATIONS, REPLENISHMENT AND PLATING RATE.

DATE	REAL TIME	TOTAL TIME (hrs)	BATH pH	NICKEL CONC. (g/l)	REPLENISH HXIR (gal)	BATH AGE (MTOs)	BATH REJUVE -NATION	BATH HYPO (g/l)	BATH ORTHO (g/l)	BLADE PLTG. RATE (mils/hr)
11/18/94	14:30	0.00	4.80	6.30						
	16:30	0.00	4.77		3.75	0.1				
11/29/94	14:30	0.00	4.86	6.25	3.75	0.2				
	17:30	3.00	4.83							0.267
	19:30	5.00	4.81							0.230
	21:35	7.08	4.84							0.212
	23:15	8.75	4.88	5.99						0.183
11/30/94	01:00	10.50	4.89	5.74	3.75	0.3				0.162
	03:00	12.50	4.75	6.13						0.137
	05:00	14.50	4.76	6.02						0.105
	08:00	17.50	4.77	5.89	3.75	0.4				0.082
	10:00	19.50	4.87	6.18						0.116
	12:00	21.50	4.91	6.30						0.136
	14:00	23.50	4.85							0.127
	16:30	26.00	4.80		3.75	0.5				
	18:30	28.00	4.86	5.69	3.75	0.6				0.130
	22:15	31.75	4.81	5.75	2.50	0.7				0.153
12/01/94	00:30	34.00	4.85	5.90						0.151
	02:15	35.75	4.82	5.72	2.50	0.7				0.155
	04:00	37.50	4.82	5.87						0.159
	06:15	39.75	4.85	5.80	2.50	0.8				0.182
	08:15	41.75	4.93	5.63	2.50	0.9				0.150
	10:00	43.50	5.00	6.00						0.174
	11:15	44.75	5.01	5.74	2.50	0.9				0.189
	13:15	46.75	5.01	5.25	2.50	1.0				0.222
	15:45	49.25	4.86	5.64	3.00	1.1				0.179
	18:10	51.67	4.73	5.69	3.25	1.2				0.197
	20:00	53.50	4.79	6.15						0.210
	22:05	55.58	4.73	5.72	3.75	1.3				0.198
12/02/94	00:15	57.75	4.75	6.03						0.159
	02:15	59.75	4.74	5.84	3.75	1.4				0.195
	04:15	61.75	4.75	6.22						0.174
	06:15	63.75	4.77	5.89	3.75	1.5				0.141
	08:15	65.75	4.73	6.60						0.182
	10:15	67.75	4.73	6.50						0.230
	12:15	69.75	4.73	6.10						0.220
	14:15	71.75	4.73	5.93						0.215
12/05/94	15:30	71.75	4.80	6.20	3.75	1.6				0.215
	18:30	74.75	4.81	5.78	3.75	1.7				0.199
	20:45	77.00		6.10						0.175
	22:45	79.00	4.72	6.04						0.156
12/06/95	00:30	80.75	4.77	5.88						0.127
	02:30	82.75	4.76	5.83						0.114
	04:30	84.75	4.76	5.69	3.75	1.8				0.100
	06:30	86.75	4.76	6.18						0.108

TABLE 2. BATH CONCENTRATIONS, REPLENISHMENT AND PLATING RATE (Continued).

DATE	REAL TIME	TOTAL TIME (hrs)	BATH pH	NICKEL CONC. (g/l)	REPLENISH HXIR (gal)	BATH AGE (MTOs)	BATH REJUVE -NATION	BATH HYPO (g/l)	BATH ORTHO (g/l)	BLADE PLTG. RATE (mils/hr)
	08:30	88.75	4.71	5.87						0.138
	10:30	90.75	4.73	5.75	3.75	1.9		25.4	37.0	0.180
	12:30	92.75	4.67	5.66	3.75	2.0				0.200
	16:30	96.75	4.71	5.40	3.75	2.1				0.217
	18:30	98.75	4.78	5.41	3.75	2.2				0.221
	20:45	101.00	4.69	5.84						0.200
	22:30	102.75	4.67	5.48	3.75	2.3				0.179
12/07/94	00:45	105.00	4.61	5.10	3.75	2.4				0.184
	02:15	106.50	4.60	5.70	3.75	2.5				0.215
	03:45	108.00	4.61	5.71	3.75	2.6				0.254
	05:15	109.50	4.60	5.91						0.253
	06:15	110.50	4.65	5.96						0.252
	08:30	112.75	4.82	5.80						0.271
	10:30	114.75	4.80	6.10	3.75	2.7				0.218
	12:30	116.75	4.67	5.80						0.189
	14:30	118.75	4.65	5.70	3.75	2.8				0.232
	16:30	120.75	4.62	6.02						0.268
	18:30	122.75	4.64	5.50	3.75	2.9				0.225
	20:30	124.75	4.70	6.40						0.210
01/18/95	09:30	124.75	4.70	6.40	11.25	3.2		33.4	76.7	0.210
	10:30	125.75	4.66							0.188
	12:30	127.75	4.70				15			0.179
	14:30	129.75	4.85	6.42	3.75	3.3				0.192
	16:30	131.75	4.76	6.64			15			0.231
	17:30	132.75	4.82		3.75	3.4				
	20:30	135.75	4.76	6.45						0.223
	22:30	137.75	4.77	6.68			15	40.1	70.3	0.238
	23:30	138.75			3.75	3.5				
01/19/95	01:00	140.25	4.78	6.24	3.75	3.6				
	02:30	141.75	4.72	6.31	3.75	3.7				
	03:15	142.50	4.73	6.79						
	05:00	144.25	4.60	7.21						
	08:00	147.25	4.57	6.48			15			0.221
	10:00	149.25	4.76	6.40	3.75	3.8				0.210
	11:15	150.50					15			0.211
	12:00	151.25	4.71	5.91	3.75	3.9	15			
	14:00	153.25	4.91	6.19	3.75	4.0	15			0.254
	16:00	155.25	4.85	7.24	3.75	4.1				0.249
	18:00	157.25	4.88	7.09				40.9	60.0	0.340
	20:30	159.75	4.82	6.82						0.333
	22:30	161.75	4.72	6.57						0.298
01/20/95	00:45	164.00	4.68	6.64						0.391
	02:30	165.75	4.69	6.24	3.75	4.2				0.381
	04:30	167.75	4.63	7.45						0.352
	06:00	169.25	4.61	6.31	3.75	4.3				0.379

TABLE 2. BATH CONCENTRATIONS, REPLENISHMENT AND PLATING RATE (Continued).

DATE	REAL TIME	TOTAL TIME (hrs)	BATH pH	NICKEL CONC. (g/l)	REPLENISH HXIR (gal)	BATH AGE (MTOs)	BATH REJUVE -NATION	BATH HYPO (g/l)	BATH ORTHO (g/l)	BLADE PLTG. RATE (mils/hr)
	08:00	171.25	4.63	6.83						0.405
	10:00	173.25	4.67	6.56			15			0.357
	13:30	176.75	4.90	6.21	3.75	4.4				0.418
01/23/95	13:00	176.75	4.95	6.46			15	39.0	74.6	0.418
	14:00	177.75	4.90	6.15	3.75	4.5				
	16:30	180.25		6.12			15			0.420
	17:30	181.25			3.75	4.6				0.420
	19:00	182.75	5.05	6.34			15			0.423
	20:30	184.25		6.58	3.75	4.7				0.412
	21:10	184.92		6.58			15			
	23:00	186.75			3.75	4.8				
	23:45	187.50		6.52						0.471
01/24/95	01:30	189.25	4.88	5.69	3.75	4.9				0.449
	03:00	190.75	4.75	6.06						0.442
	04:30	192.25	4.74	5.69	3.75	5.0				0.405
	06:00	193.75	4.73	6.42						0.379
	08:00	195.75	4.78	5.55	3.75	5.1				0.291
	09:30	197.25	4.91	5.21	7.50	5.3				0.344
	12:00	199.75	4.71	6.22						0.300
	14:00	201.75	4.71	6.96			15			0.305
	16:00	203.75	4.69	6.22	3.75	5.4	15			0.265
	18:00	205.75	4.81	6.54	3.75	5.5				0.235
	20:30	208.25	4.80	6.09			15	40.5	82.2	0.195
	23:00	210.75	4.84	6.04	3.75	5.6				0.236
	23:30	211.25	4.92	5.74	3.75	5.7				
01/25/95	01:00	212.75	4.80	6.02	3.75	5.8				0.250
	03:00	214.75	4.62	5.17	3.75	5.9				0.300
	04:00	215.75	4.44	5.56	3.75	6.0				0.310
	06:00	217.75	4.35	5.16	3.75	6.1				0.311
	08:00	219.75	4.44	4.70	3.75	6.2	15			0.256
	08:45	220.50	4.29	5.20	3.75	6.3	15	38.3	72.7	0.239
03/28/95	14:00	220.50	4.83	6.72		6.3	15	38.3	72.7	
	16:00	222.00	4.90	6.68	3.75	6.3	15			0.375
	18:00	224.00	4.93	6.80						0.350
	20:20	226.33	4.90	6.96						0.324
	22:00	228.00	4.82	6.28	3.75	6.4	15			0.338
03/29/95	00:30	230.50	4.99	6.80						0.333
	02:00	232.00	4.94	5.97	3.75	6.5				0.317
	03:45	233.75	4.92	6.10	3.75	6.6				0.320
	05:30	235.50	4.84	6.25	3.75	6.7				0.342
	08:00	238.00	4.80	6.50						0.367
	10:15	240.25	4.73	6.23	3.75	6.8	15			0.363
	12:00	242.00	4.80	6.21	3.75	6.9				0.357
	14:00	244.00	4.65	6.31	3.75	7.0				0.363
	16:00	246.00	4.65	6.70						0.369

TABLE 2. BATH CONCENTRATIONS, REPLENISHMENT AND PLATING RATE (Continued).

DATE	REAL TIME	TOTAL TIME (hrs)	BATH pH	NICKEL CONC. (g/l)	REPLENISH HXIR (gal)	BATH AGE (MTOs)	BATH REJUVE -NATION	BATH HYPO (g/l)	BATH ORTHO (g/l)	BLADE PLTG. RATE (mils/hr)
	18:15	248.25	4.85	6.74	3.75	7.1	15	41.87	78.25	0.366
	20:30	250.50	4.74	6.32						0.357
	22:30	252.50	4.73	6.04	3.75	7.2				0.358
03/30/95	00:30	254.50	4.82	6.42						0.354
	02:00	256.00	4.81	6.21	3.75	7.3				0.347
	03:45	257.75	4.85	6.93						0.350
	05:45	259.75	4.81	6.29	3.75	7.4				0.355
	08:00	262.00	4.72	6.83						0.375
	10:00	264.00	4.69	6.79				38.93	80.67	0.374
	12:00	266.00	4.75	6.40	3.75	7.5	15			0.372
	14:00	268.00	4.89	6.70						0.373
	16:00	270.00	4.85	6.06	3.75	7.6				0.380
	18:00	272.00	4.98	6.70						0.377
	20:00	274.00	4.93	6.46	3.75	7.7	15			0.375
	22:00	276.00	5.06	6.00	3.75	7.8				0.379
03/31/95	00:00	278.00	5.01	6.57						0.383
	02:00	280.00	5.00	6.35						0.380
	04:00	282.00	4.98	5.96	3.75	7.9				0.373
	05:30	283.50	4.75	5.94	3.75	8.0		36.89	89	0.370
	07:30	285.50	4.92	5.98	3.75	8.1				0.371
	10:15	288.25	4.75	6.04	3.75	8.2				0.365
	12:00	290.00	4.75	6.43						0.363
	14:00	292.00	4.82	6.28				38.51	90.2	0.363
04/03/95	15:00	292.00	4.75	5.88	3.75	8.3	15			0.363
	17:00	294.00	4.84	6.42						0.359
	19:00	296.00	4.90	6.26	3.75	8.4				0.357
	21:00	298.00	4.84	6.30	3.75	8.5				0.356
	23:00	300.00	4.77	6.71						0.356
04/04/95	01:00	302.00	4.80	6.74						0.357
	03:00	304.00	4.79	6.40						0.349
	05:00	306.00	4.80	6.26	3.75	8.6				0.345
	06:30	307.50	4.75	6.73						0.342
	07:45	308.75	4.70	6.68			15			0.344
	10:00	311.00	4.78	6.74						0.341
	12:00	313.00	4.74	7.08						0.335
	14:30	315.50	4.70	6.32	3.75	8.7				0.335
	16:00	317.00	4.75	6.73				35.3	96	0.336
	18:00	319.00	4.74	6.44						0.334
	20:35	321.58	4.83	6.24	3.75	8.8				0.330
	22:00	323.00	4.85	6.70						0.330
04/05/95	00:15	325.25	4.87	6.48						0.324
	02:15	327.25	4.87	6.21	3.75	8.9				0.321
	04:15	329.25	4.84	6.44						0.319
	06:00	331.00	4.84	6.51						0.318
	08:00	333.00	4.85	6.27	3.75	9.0				0.317

TABLE 2. BATH CONCENTRATIONS, REPLENISHMENT AND PLATING RATE (Continued).

DATE	REAL TIME	TOTAL TIME (hrs)	BATH pH	NICKEL CONC. (g/l)	REPLENISH HXIR (gal)	BATH AGE (MTOs)	BATH REJUVE -NATION	BATH HYPO (g/l)	BATH ORTHO (g/l)	BLADE PLTG. RATE (mils/hr)
	10:00	335.00	5.00	6.18	3.75	9.1	15			0.322
	12:00	337.00	5.00	6.48						0.322
	14:00	339.00	4.92	6.09	3.75	9.2				0.322
	16:00	341.00	4.85	6.73			15			0.321
	18:00	343.00	5.06	5.93	3.75	9.3				0.322
	20:45	345.75	5.02	6.25	3.75	9.4				0.323
	22:00	347.00	4.98	6.41				32.2	93.2	0.326
04/06/95	00:30	349.50	4.95	6.27	3.75	9.5	15			0.324
	02:30	351.50	4.94	6.48						0.324
	04:30	353.50	4.96	6.47						0.323
	06:00	355.00	4.93	6.25	3.75	9.6				0.323
	08:00	357.00	4.89	6.21	3.75	9.7				0.323
	10:00	359.00	4.85	6.84						0.324
	12:00	361.00	4.84	6.57						0.325
	14:00	363.00	4.81	6.60			15			0.326
	16:00	365.00	4.97	5.99	3.75	9.8				0.327
	18:00	367.00	5.00	6.13	3.75	9.9				0.328
	20:00	369.00	4.93	6.43						0.330
	22:00	371.00	4.95	6.18	3.75	10.0		32	97.6	0.330
04/07/95	00:00	373.00	4.96	6.58						0.327
	02:00	375.00	4.95	6.49						0.330

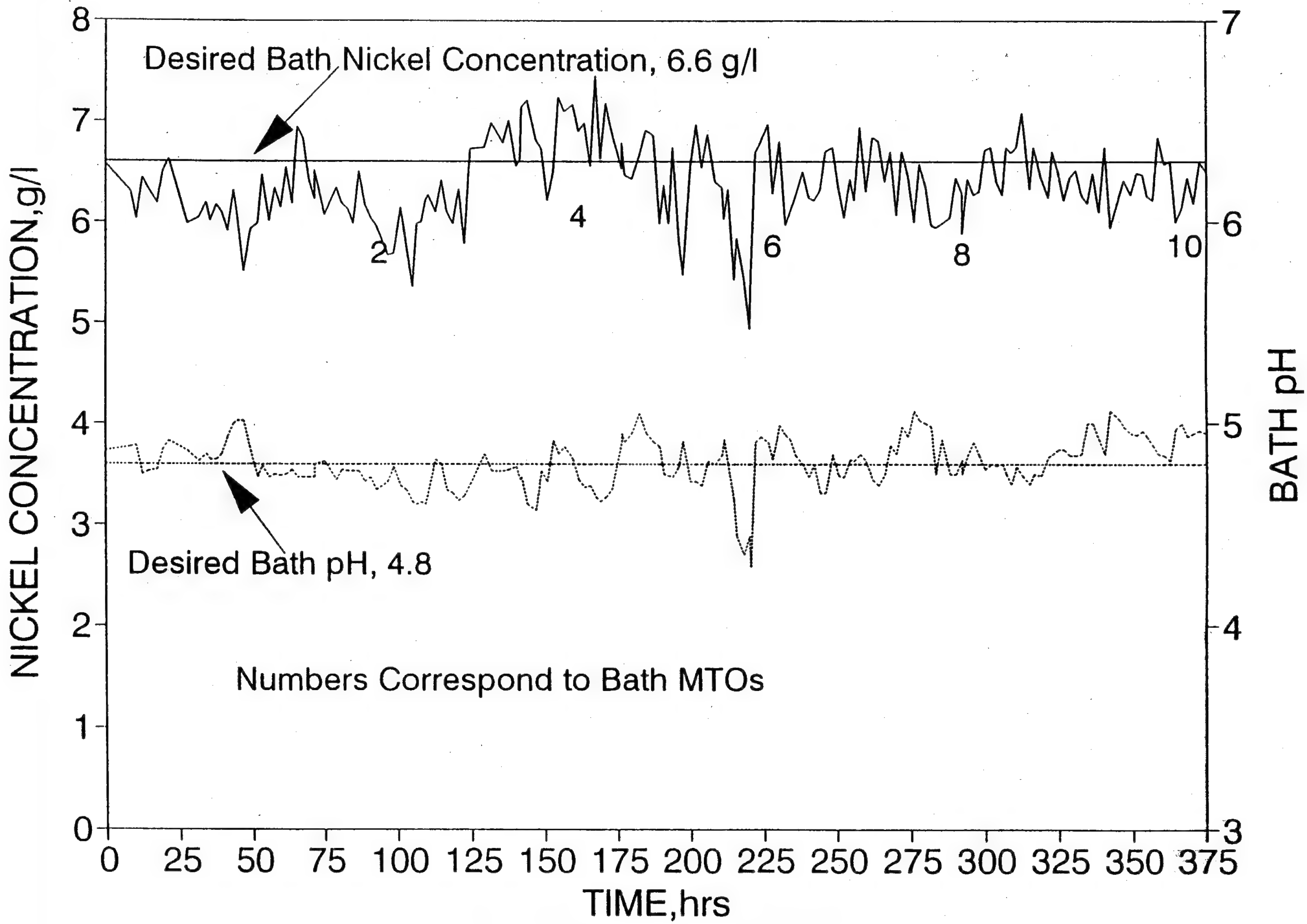

Figure 3. Bath Nickel Concentration and pH.

ICAP (Inductively Coupled Argon Plasma) analysis of bath nickel showed that colorimeter measurements were accurate and it is an efficient measurement of bath nickel concentration. Furthermore, it is not affected by the presence of calcium in the bath and represents the true nickel content of the bath.

The desired bath pH is 4.8. Prior to bath rejuvenation the pH was maintained by adding 50 percent ammonia to the bath either manually or using the PU-2 ammonia pump. Once the rejuvenation started, the ammonia additions were infrequent since the bath was self-regulating with respect to the pH because of the return of high pH treated bath solution to the bath. The bath pH as a function of time is shown in Table 2 and Figure 3. As shown, the bath pH was maintained substantially in the 4.6 to 4.9 range during the entire demonstration period, except during the sixth MTO which is discussed later. If anything, the bath pH tended to stay above 4.8. This is due to two reasons; (a) the make-up water (to take care of evaporation losses) was substantially alkaline (pH of 7.8) and (b) bath loading was small most of the time resulting in low H^+ ion production in the bath. In the future, it is suggested that hypophosphorus acid be available to reduce the pH if necessary. Bath pH needs to be below 4.8 when a batch of rejuvenated solution (at a pH of 9) is added to the bath.

B. BATH ANION CONCENTRATIONS

Bath hypophosphite concentration should be in the range of 34 to 40 grams/L to obtain the 10 percent phosphorous content in the deposit. Bath hypophosphite is replenished whenever nickel replenishment is made since the replenishment is nickel hypophosphite. During the 10 MTOs of plating, bath hypophosphite was measured fourteen times and the values are shown in Table 2. Bath hypophosphite had a low value 25 grams/L initially (at 1.8 MTOs), but reached a steady state value of 40 grams/L by 3 MTOs and remained at that level almost all the time. At the end of testing (10 MTOs), it was drifting lower to a value of 32 grams/L.

The primary function of the Stapleton PU-2 EN bath rejuvenation unit is to remove the baths only contaminant, the orthophosphite ion by periodically treating 10 percent of the bath. Bath rejuvenation was initiated after the bath was at 2.8 MTOs and the orthophosphite level was at 77 grams/L. The goal was to maintain the orthophosphite level between 2 MTOs (60 grams/L) and 3.5 MTOs (105 grams/L). Bath orthophosphite concentration was measured periodically by iodometric titration. The orthophosphite values are given in Table 2 and are shown graphically in Figure 4. As shown in Figure 4, the PU-2 unit was very effective in removing orthophosphite from the bath and

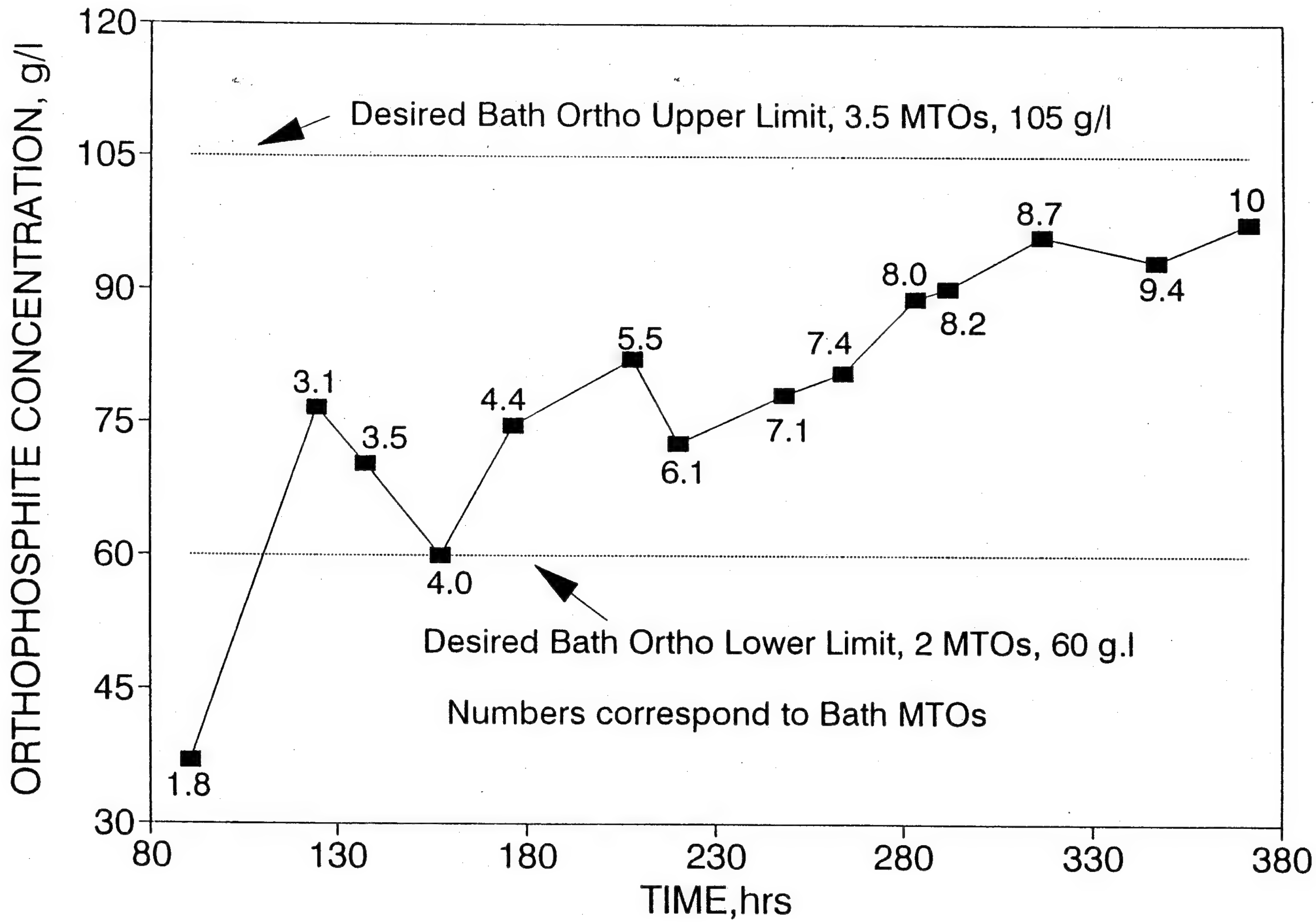

Figure 4. Bath Anion Concentrations.

the bath was maintained between an orthophosphite equivalent of 2 to 3 (between 60 and 90 grams/L) MTOs during the entire demonstration period. As given in Table 2, a total of 30 treatments were performed during the time the bath age increased from 2.8 MTOs to 10 MTOs; i.e., about 5 treatments per one MTO. Since the bath orthophosphite content was essentially between 2 and 3 MTOs, and 10 percent of the bath is treated every time, each treatment removes orthophosphite equivalent to 0.2 MTOs and 5 treatments per MTOs is the expected and recorded frequency. It can be concluded that the PU-2 rejuvenates the bath in an effective manner.

Based on experience gained from the demonstration, it is recommended that the bath be maintained closer to 3 MTOs equivalent of orthophosphite (instead of the original intention of maintaining near 2 MTOs equivalent) and add calcium hydroxide that is less than the stoichiometrically required amount necessary to precipitate all the orthophosphite in the batch being treated. This ensures that all the calcium reacts to form calcium orthophosphite and no unreacted calcium hydroxide fines enter the bath. In addition, fewer bath rejuvenations are needed per MTO and the plating rate does not seem to be affected by the slightly increased orthophosphite concentration.

C. PLATING RATE

The expected plating rate, based on laboratory testing, is 0.35 mils/hr (single-sided), which is 25 to 50 percent higher than for conventional baths because of byproduct build-up in conventional baths. The plating rate is measured by monitoring the thickness of razor blades attached to the dummy panels (and parts) in the bath. The plating rate is measured every 2 hours and the measured plating rate is given in Table 2 and shown graphically in Figure 5. It should be noted that the values correspond to a 10-hour moving average since the 2-hour values are sometimes erroneous due to the small increments in thicknesses being measured.

During the first 2 MTOs of plating, the rate was substantially lower at 0.15 mils/hr. This was due to an imbalance in the bath replenisher to bath control additive caused by fouling of the bath replenisher feed line by sedimented nickel hypophosphite crystals in the replenisher drum. After this was corrected, the plating rate increased to 0.25 mils/hr during the third and fourth MTOs. The lower rate was traced to incorrect formulation of the bath control additive for the type of plating at Tinker AFB (see Section IV). Once the reformulated control additive was introduced into the bath, the plating rate slowly increased to the expected value of 0.35 mils/hr (by 4 MTOs of plating) and

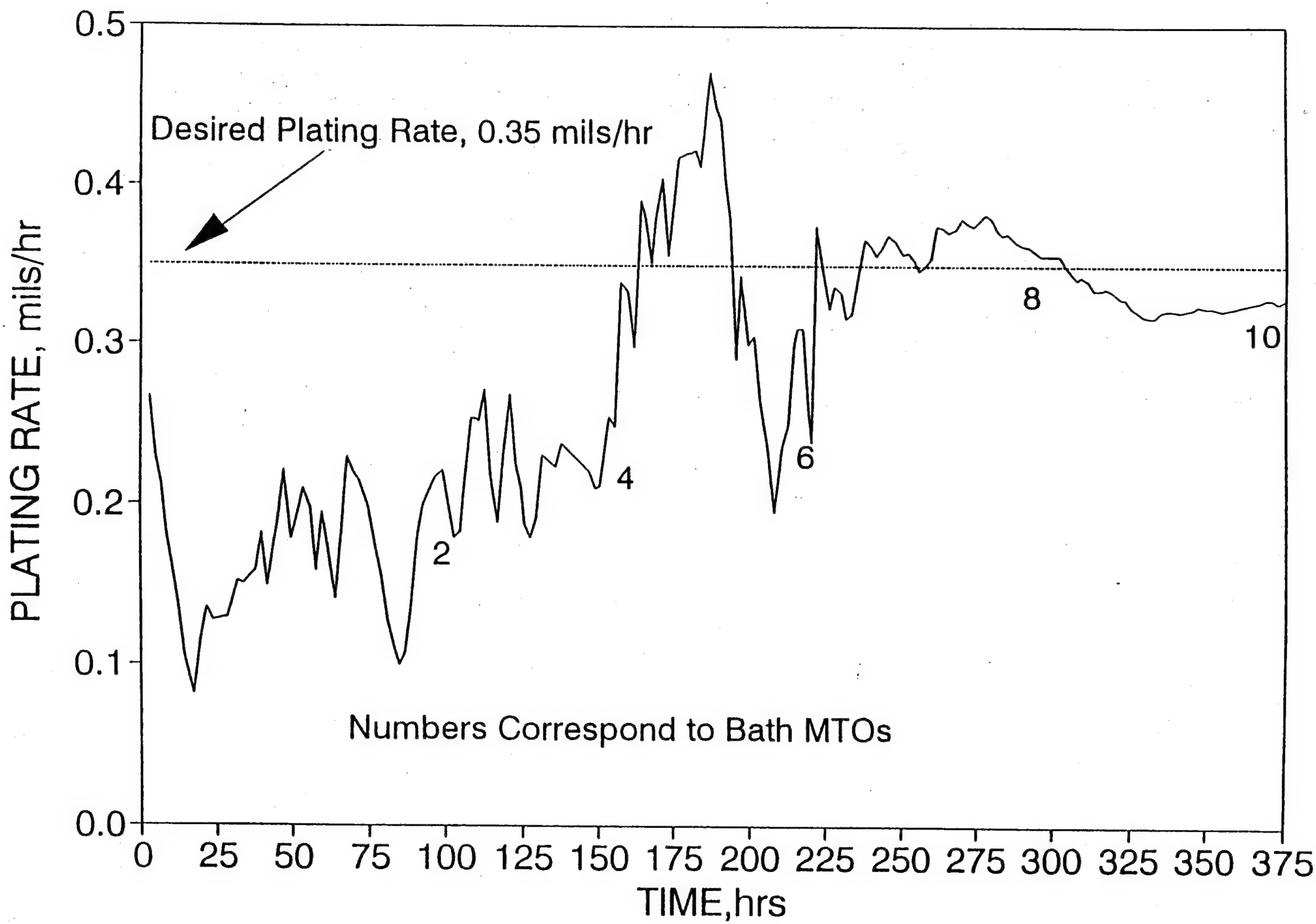

Figure 5. Bath Plating Rate.

remained at or above that rate till 5 MTOs of plating. Then the plating rate decreased to 0.25 mils/hr because of decrease in bath nickel concentration and bath pH (see Figure 3). This is discussed below.

After the mechanical modifications were completed after the sixth MTO and the bath restarted, the plating rate immediately went up to 0.35 mils/hr and stayed at that level until the end of prototype demonstration (i.e., 10 MTOs). Based on these results, it can be concluded that the bath plates at 0.35 mils/hr under normal conditions. On the other hand, in a conventional bath, which has a life of 3 to 5 MTOs, the average rate of plating after the first, second, third, and fourth MTOs are 0.5, 0.4, 0.28, and 0.23 mils/hr, respectively (Tinker AFB data from 1/30/95 to 2/28/95).

D. PLATING QUALITY

Plating quality was acceptable during the first 4 weeks of plating (up to 5 MTOs). There were no visual signs of pitting on the parts. There was some surface roughness on the horizontal sections of the parts. However, this was not considered as detrimental to the part usage, since it will be removed during the subsequent machining. This type of surface roughness was also observed during laboratory testing and was judged acceptable by OC-ALC. During the last week of initial 5-week testing, about 16 hours after resumption of plating, the filter in the PU-2 bath rejuvenation unit developed a leak in one corner and some filter cake (calcium orthophosphite) particles mixed with the filtrate. Although there is a bag filter in the filtrate holding tank that acts as a secondary containment to remove any filter cake particles from the filtrate under normal circumstances, excessive breakage of filter cake caused the bag filter to plug and filter cake particles overflowed into the filtrate holding tank. During the subsequent rejuvenation, the filtrate containing the filter cake particles entered the bath. This raised the calcium content of the bath beyond its solubility limit.

The calcium orthophosphite particles in the bath set off a chain of events detrimental to EN plating. Some of the particles deposited on the parts being plated forming a calcium film on the surface leading to unacceptable plating quality. The particles also became a large source of new plating surface for the bath. Electroless nickel deposited on these particles causing nickel concentration as well as pH to drop below acceptable levels during the last MTO of plating despite frequent replenishments (see Figure 3). The low pH in the bath caused the plating rate to drop below the desired 0.35 mils/hr to 0.25 mils/hr. Eventually the calcium particles became heavy because of EN deposition on them and sank to the tank bottom. Meanwhile, the filter leak was repaired and filter performance was tested satisfactorily with a few rejuvenations. In addition to the filter leak

repairs, several mechanical modifications were made to the PU-2 Unit (see Section IV C, Mechanical Modifications to the PU-2 Unit). During the modifications, bath solution was stored in drums.

Subsequent bath analysis showed that calcium content of the bath is within its solubility limit and the bath solution is clean. When the bath solution was transferred to drums for storage, the tank bottom had a substantial amount of "seed-out" or "plate-out." In essence, the bath cleaned itself by plating out all the suspended calcium particles.

After the completion of mechanical modifications, plating was resumed, first with coupons and later with real parts. Plating was continued until 10 MTOs at which time the demonstration was concluded.

Plating quality was acceptable throughout the demonstration except during the sixth MTO (because of calcium deposition caused by filter leak). All parts and coupons were visually inspected to ensure pit-free plating. In addition, plated coupons (with 10, 20, 30, 40, and 50 mil thick deposits) were given to OC-ALC personnel so that they can perform grindability tests. Another criterion for plating quality is the phosphorous content of the Ni-P deposit. Five samples of the deposit (at 5, 6, 8, 9, and 10 MTOs) were analyzed by Battelle (using ICP) for their phosphorous content. All samples showed more than the required 10 percent phosphorous and the phosphorous content values were in the range of 10.04 to 11.29 weight percent phosphorous.

E. FILTER CAKE GENERATION AND NICKEL CONTENT

The only waste generated from Stapleton EN process is the calcium orthophoshite filter cake. During the bath rejuvenation sequence, the calcium orthophosphite cake is filtered from the treated bath solution. After the filtrate removal, the cake is spray rinsed with water to remove most of its nickel content by washing out the plating solution. The filter cake is then collected in a bin. During the 10 MTOs of plating, a total of 30 bath rejuvenations were performed. It is estimated that approximately 488 pounds of dry cake ($\simeq$976 pounds of wet cake, < two 55-gallon drums) was generated and collected. Seven samples of the filter cake were taken at various times and analyzed for the solids content, nickel content (by ICP) and for nickel by toxicity characteristic leachage procedure (TCLP). These results are given in Table 3. The cake solids percent was in the 50 percent range, which was the expected value. The nickel content (wet basis) varied from 1000 to 2000 ppm. The variation is due to improper operation of spray rinse caused by lack of water pressure in the line (see Section IV). These nickel content values are lower than those obtained in the bench-scale tests. Assuming an average value of 1500 ppm nickel (wet basis), the nickel utilization

by the Stapleton EN process is about 98.1 percent compared to 75 percent nickel utilization in a conventional EN process where the bath is dumped after 4 MTOs. This means that there is a 93 percent reduction in the amount of nickel discharged from the plating operation through the pretreatment system.

TABLE 3. FILTER CAKE ANALYSIS

Sample Date	Bath Age (MTOs)	Cake Solids %	Cake Ni Content (ppm)	Cake TCLP Ni (ppm)
1/18/95	2.8	48	2119	50.2
1/19/95	3.8	50	1746	19.2
1/20/95	4.5	41	1004	30.9
1/25/95	6.1	53	1002	24.1
4/4/95	8.6	54	1168	54.9
4/5/95	9.2	52	1506	69.2
4/6/95	10.0	51	1418	46.2

The nickel discharge can be further reduced by further washing of the filter cake as was demonstrated in the laboratory tests. However, during a presentation to OC-ALC and Environics in May, 1994, it was suggested by OC-ALC that the washing step be eliminated as they already had a system set-up to dispose of solid waste. Furthermore, if washing becomes important in the future, it can always be added to meet future nickel discharge reduction goals.

F. DISCUSSION OF OVERALL PERFORMANCE OF THE PROTOTYPE

Relative to the operational goals for the prototype demonstration, the performance of the PU-2 unit was satisfactory. Specifically, 10 MTOs of plating was completed, plating rate of 0.35 mils/hr was attained and maintained at that rate. Plating quality was acceptable (except during the sixth MTO due to filter leak) with pit-free plating and greater than 10 percent phosphorous content in the deposit. Bath rejuvenation was very effective in maintaining the bath orthophosphite level between 2 and 3 MTOs equivalent. There were problems during the demonstration; but these were mostly mechanical and not process-related. Mechanical problems are expected during any prototype start-up. Once

these mechanical problems were fixed via equipment modifications, the equipment performed without any further problems. All parts of the unit such as the reactor/agitator, vacuum filter, pumps, and the system controls performed as per expectations resulting in the proper performance of the bath and the bath rejuvenation system.

Although the testing demonstrated trouble-free operation of the unit, it should be noted that the unit is an engineering prototype and not a production unit. Additional equipment modifications and design changes are necessary to implement this as a production unit at other ALCs.

Specifically, a smaller unit capable of treating 50-gallon EN baths is desirable at ALCs. In addition, if vacuum filtration is replaced with pressure filtration mechanism, the treatment (bath rejuvenation) cycle time will be reduced substantially and even a smaller unit can handle larger EN baths (e.g., 150-gallon). The other design modification that is suggested is the use of tighter filter cloth in the primary filter to ensure particle-free filtrate returning to the bath.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

Based on 7 weeks of prototype testing, the following conclusions can be drawn regarding the Stapleton Enfinity EN process:

(1) Stapleton EN bath chemistry and rejuvenation prototype is very effective in removing the orthophosphite contaminant from the bath and maintaining the bath composition to eliminate bath dumps.

(2) After some initial adjustments, the plating rate reached the desired goal of 0.35 mils/hr. The plating quality is acceptable with pit-free plating and at least 10 percent phosphorous content in the deposit.

(3) Bath age at the conclusion of prototype demonstration was 10 MTOs while a conventional EN bath would have been dumped at 4 MTOs of age.

(4) There were a number of mechanical malfunctions in the equipment during the demonstration period. These may be considered start-up problems. Mechanical modifications have been made by the vendor and Battelle to address these problems and to ensure trouble-free operation.

(5) The nickel utilization using the Stapleton bath rejuvenation process is 98.1 percent compared to 75 percent using a traditional EN bath, i.e., nickel discharge from EN plating is reduced by 93 percent.

Based on the prototype demonstration results, it is concluded that Stapleton EN baths rejuvenation system (especially after the design and equipment modifications suggested above) is an attractive alternative to conventional EN plating.

APPENDIX A

SPECIFICATION FOR BID

September 30, 1993

Lieutenant Phil Brown
Headquarters Air Force Civil
Engineering Support Agency
Research and Acquisition Division
HQ AFCESA/RAVS
Tyndall AFB, FL 32403-5000

Subtask 4A Electroless Nickel Rejuvenation Plant Design
Task V, Contract F08635-90-C-0064

Dear Lieutenant Brown:

With this letter we are submitting a copy of the "Specifications For Bid" for the "Electroless Nickel Plating Bath Rejuvenation Process" scaleup and demonstration unit to allow procurement of same. We anticipate the issue of a purchase order by October 8, 1993, with the expected delivery of the unit at Tinker AFB, OK-ALC within 14 weeks of issuing the purchase order. We also anticipate design drawings within 6 weeks of the purchase order.

We are continuing to investigate a filter cake wash system design to allow a final filter cake for disposal that contains less than 5 ppm nickel (by TCWP), the expected EPA regulatory limit. The filtrates from washing can be recycled either to the bath or a rinse tank.

If you have any questions about this report, please call me at 614-424-4812, or Mr. Ted Tewksbury at 614-424-6409.

Very truly yours,

Satya P. Chauhan
Director
Process Systems & Separations Technology

SPC:dmk
Enclosure
cc: AFDTC-PKRA (Attn: Mr. L. Turner)
Mr. Tom Walker, Tinker AFB
Mr. Glenn Graham, Tinker AFB

SPECIFICATIONS
FOR
ELECTROLESS NICKEL PLATING BATH REJUVENATION PROCESS

Process Description

The U.S. Air Force uses electroless nickel plating baths at Tinker Air Force Base. The type of bath used at Tinker is an acidic hypophosphite-based bath. During this plating process, reaction byproducts such as orthophosphite, sodium or sulfate accumulate in the bath to a level that interferes with the plating reaction and the bath requires dumping. These baths, when dumped, constitute a major source of hazardous waste for disposal. Battelle has conducted an extensive evaluation of several candidate processes to demonstrate removal of electroless nickel by-products to extend the bath life. The evaluation was funded by the U.S. Air Force. A process, Stapleton Enfinity, with some modifications, was recommended for full-scale prototype demonstrations at the conclusion of this study. At this time, Battelle and the Air Force are seeking bids for installation of a prototype of this process at Tinker AFb, OK-ALC.

Process Specifications

The rejuvenation (purification) unit is required to treat at least 30-gallons of electroless nickel bath contaminated solution per cycle, with a maximum cycle time of 3 hours. An additional requirement is automatic start of the filtering step to prevent or minimize nickel plating in the treatment reactor as well as automatic start of the spray wash cycle to the filter (after the electroless nickel bath solution has been filtered) to displace any plating solution adhering to the cake. Due to the lack of space available near the electroless nickel plating baths at Tinker, the unit should be skid-mounted and as compact as possible. The footprint of the unit should not exceed 7 feet by 4 feet by 6 foot height. The available utilities are 110 VAC, 100 psi air, deionized water and cooling water.

Equipment Specifications

- All pumps to be air-operated diaphragm
- Reactor to be 316 stainless steel (30-gallons)
- All electrical fixtures to be NEMA 4
- All equipment to be skid-mounted
- Skid and steel framework to be epoxy-painted
- System to be totally prepiped and wired
- Controls and monitor to be skid-mounted or optionally remote mount
- Tanks and piping to be CPVC, poly-propylene, kynar or 316LC stainless steel
- Air, water and cooling water connections to be NPT.

Tinker AFB-OKALC Specifications

The process shall be designed, constructed, and installed in accordance with all mechanical and electrical specifications of Tinker AFB-OKALC that apply (copy attached).

Equipment and Design Delivery

Receipt of the equipment at Tinker AFB, OK-ALC will be within 14 weeks after receipt of purchase order from Battelle. Receipt of the design drawings at Battelle within 6 weeks after receipt of Purchase order.

Equipment Installation

At least 3 man-days of engineering assistance at Tinker AFB, OK-ALC shall be included in the bid to assist with equipment installation and system start-up. Note: An additional separate proposal is requested for engineering services at Tinker AFB, OK-ALC to assist in start-up and operator training on an as-needed basis. This proposal should be quoted as cost per man-day of engineering services.

Equipment/Process Warranty

The proposal should delineate any warranties including manufactures warranties that will be passed along to the Air Force as owners.

Manuals

The contractor will supply 6 copies of installation/operation manuals to the Air Force and one (1) copy for Battelle at time of equipment delivery. The manuals will include, as a minimum, step by step installation instructions, start-up, operating and shut-down procedures. The manual will also include a process flow diagram of the process, a piping and installation diagram, and a 1-line electrical drawing. A recommended spare parts list should also be included.

Payment Schedule and Acceptance Criteria

Payment on the above procurement will be as follows:

- 25 percent of purchase price 6 weeks after issue of purchase order, and receipt of design drawings.
- 50 percent of purchase price upon delivery to Tinker AFB-OKALC.
- 25 percent of purchase price upon acceptance of operating unit by Battelle and the Air Force.

Acceptance criteria will be the mechanical operation of all components of the system as designed. Acceptance criteria will be considered to be met if undue delays are caused by either Battelle or the Air Force.

APPENDIX B

SUMMARY OF PU-2 OPERATING AND SERVICE MANUAL

STAPLETON TECHNOLOGIES Inc.
1350 W 12th Sreet
Long Beach, California 90813
(800) 266-0541 (310) 437-0541
FAX (310) 437-8632

ENFINITY PU-2

DAILY OPERATING PROCEDURES

INTRODUCTION

This short document is provided for the operators of the PU-2 ENFINITY equipment. A complete description of the maintenance and operations is available in the Operating Manual.

PREVENTIVE MAINTENANCE

These are actions which need to be taken on a regular basis to maintain the equipment. They are organized by services and are ordered by frequency.

---

1. Demineralized Water, Service, Daily
1.1. Check that Demineralizer water pressure is up and the pump is running.
1.2. Check and set valve G, Di Supply, to the ON position.

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2. Air, Services, Weekly
2.1. Check Air Supply trap and drain if required.
2.2. Check lubricator and add WD-40 to fill line.
2.3. Check operations of all pneumatic equipment by manually pressing each pilot air valves on the MAC air manifold. It is recommended that the pneumatic equipment be operated for no longer than 3 seconds to prevent material loss.

---

3. Cooling Water, Services, Weekly
3.1. Check the cooling water flow by adjusting the temperature set point to below room temperature. The cooling system will initiate flow of cooling water through the reactor shell. The agitator should be operating and the water draining onto the floor.

---

4. Filter Support
4.1. Check the bag filter in the recovery tank, Replace with 1 micron bag daily.
4.2. Check the cartridge filter for solids, Replace with 1 micron filter. This should be done after 10 treatments.
4.3. Check main filter membrane for tears and holes. The filter can be washed when in the UNLOAD position. This should be done monthly.

OPERATOR INSTRUCTIONS

5. Process Operations

5.1. Analysis,

5.1.1. Check the process for nickel using the HACH colorimeter. The Nickel concentration should be between 6.0 to 6.7 g/l. A 10% addition is required if the nickel is below 6.2 g/l. The tank level and the amount of evaporation will effect the observed concentration of nickel and the normalized concentration for 150 gallons. This test is performed every 2 hours.

5.1.2. Check the process for pH using a meter. This test is performed every 2 hours.

5.1.3. Check the process for Orthophosphite. This should be done weekly.

5.1.4. Check the process for Hypophosphite. This should be done weekly.

5.2. Replenishment Normal Operations, 1 + MTO, Ortho >50 g/l

5.2.1. Conditions prior to Replenishment, Check to see that the following conditions are met:

5.2.1.1. Service ON, Air, Electricity

5.2.1.2. Reactor Level LOW

5.2.1.3. Recovery Tank FULL

5.2.1.4. There is more than 5 gallons of Replenisher, HXIR, available.

5.2.1.5. There is more than 1 gallon of Control, HXIC, available.

5.2.1.6. There is Ammonium hydroxide solution, 1:2 with Di water, available.

5.2.2. Operator Presses ADDITION button on front panel. From this point forward the equipment will operate automatically for several minutes. The following sequence of actions are completed by the PU2.

5.2.2.1. Removal, working solution, 15 Gallon is removed from the plating tank and delivered to the reactor. The cooling system will automatically activate when the temperature is above 100 (F). next;

5.2.2.2. Recovery, treated solution, 16 Gallons is pumped from the recovery tank to the plating tank. and;

5.2.2.3. Replenisher, HXIR, 3.75 gallons is pumped to the plating tank. and;

5.2.2.4. Control, HXIC, 570 ml, are pumped to the plating tank. and;
5.2.2.5. Ammonium hydroxide, 800 ml, are pumped to the plating tank.

5.3. Replenishment, Orthophosphite < 50 g/l. This condition is when the solution is low in orthophosphite and no treatment is required. It can also be used when there is an equipment condition which prevents the operation of the reactor and vacuum filter.

5.3.1. Conditions prior to Replenishment which must be accomplished.
5.3.1.1. Service ON, Air, Electricity
5.3.1.2. Replenisher HXIR > 5 GALLON
5.3.1.3. Control, HXIC is available for feed
5.3.1.4. Ammonium hydroxide solution 2:1 is available for feed

5.3.2. Operator Presses the ADDITION button. The feed pumps are automatically operated and the following sequence of activities and completed.
5.3.2.1. Replenisher, HXIR, 3.75 gallons is pumped to the plating tank. and;
5.3.2.2. Control, HXIC, 570 ml, are pumped to the plating tank. and;
5.3.2.3. Ammonium hydroxide, 1800 ml, are pumped to the plating tank.

---

6. Treatment of removed solution - After standard replenishment the reactor will be full of hot ENFINITY solution. After cooling in the reactor the READY to TREAT light will be on. This is the operator indicator that a treatment can proceed.

6.1. Equipment Conditions required before treating the solution.
6.1.1. Check the reactor level, it should be 15 gallons. A small black mark on the temperature probe in the reactor indicates the correct level.
6.1.2. Check the vacuum filter and unload if required.
6.1.3. Check for air pressure on the gages on the MAC unit.
6.1.4. Get bag of Purifier.

6.2. Making the Treatment
6.2.1. Press the TREAT button, The treatment will proceed automatically
6.2.2. As soon as the process starts add 6.5 pounds of Purifier to the reactor. Material should be added to the center and reactor slowly.

6.2.3. The treating of the ENFINITY process involves the following steps:
6.2.3.1. Digestion, 4 minutes, Material is circulated through the piping and back to the reactor. During the digestion segment the pH is sampled and displayed on the front panel.
6.2.3.2. Transfer, 2 minutes, The solution is pumped from the reactor to the filter. The pH probe is washed and the main vacuum pump starts the filtration.
6.2.3.3. Filtration, 7 to 15 minutes, The material is filtered by vacuum. This removes the liquid from the filter cake and produces a dry filter cake.
6.2.3.4. Rinse, 2 1/2 minutes, The vacuum will reduce as the filter cake dries. When the vacuum goes below 20 "Hg, the spray rinse is activated and rinse water is sprayed onto the filter cake. This causes the vacuum to rise again as the air is prevented from entering the cake.
6.2.3.5. Dry, 15 minutes, The vacuum pump continues to dry the cake until the remaining rinse water is removed. At this point the vacuum is below 5"Hg.
6.2.3.6. Finish Alarm, The last step in the treat process shuts down the power and lights the READY TO UNLOAD light.

6.3. Unload/Return

6.3.1. Conditions before Unload can proceed
6.3.1.1. The filter cake waste container must be in position to accept the cake when dumped.

6.3.2. UNLOAD, After the treatment process is complete the filter must be unloaded. This is accomplished by pressing the UNLOAD button. The filter chamber is raised by and air cylinder and the filter cake is allowed to fall into the container.

6.3.3. RETURN, After the filter cake is unloaded and the membrane clear the RETURN button is pushed and the filter chamber will return to the rest position.

7. CALIBRATION SETTINGS

7.1. Timer Blocks

The following values have been established in the timer blocks of the PU-2 Unit.

Pump out of REMOVAL	356 sec.
Pump of RETURN	320 sec.
Replenisher, HXIA	230 sec.
Control, HXIC	27 sec.
Ammonium hydroxide	65 sec.
Digestion,	240 sec.
Recirculate	120 sec.
Transfer	230 sec.
Dry Cake	900 sec.

7.2. Vacuum Gages

There are three vacuum gages which control the system. The high level is used to initiate the rinsing program while the low is used to shut down the process when the cake is dry.

7.3. Temperature

The temperature is set to 100 (F) and the output is used by the computer program to determine when the reactor cooling system should operate.

7.4. pH

The pH meter should be calibrated every month to insure proper operations. Follow the instructions in the manual to calibrate for operations in the 4.0 to 9.0 range. The pH value is used to alert the operator of a possible problem but has no control function.

APPENDIX C

PROTOTYPE DEMONSTRATION TEST PLAN

DRAFT
TEST PLAN FOR INSTALLATION, START-UP AND DEMONSTRATION OF THE STAPLETON ELECTROLESS NICKEL REJUVENATION SYSTEM

Tinker Air Force Base performs electroless nickel plating on aircraft parts to enhance their corrosion resistance. Traditionally, electroless nickel plating baths are dumped frequently due to the build-up of orthophosphite by-product in the bath, which alters the deposit characteristics and decreases the plating rate. U.S. Air Force contracted Battelle Memorial Institute (Battelle) to find, test, evaluate, and install a technology to rejuvenate electroless nickel baths. Battelle tested and evaluated several technologies and recommended the Stapleton electroless nickel bath rejuvenation system (Stapleton EN) for installation at Tinker AFB. Upon U.S.A.F. approval, the Stapleton EN system is scheduled for installation at Tinker AFB after the completion of plating shop modifications at Tinker AFB. This report details the performance test plan to monitor the performance of the Stapleton EN plating as well as the bath rejuvenation system.

TEST OBJECTIVES

The objectives of the test program are:

(1) Mechanical shakedown of the bath rejuvenation system

(2) Start-up of the Stapleton EN plating bath and monitoring of the bath plating characteristics and deposit characteristics through 6 metal turnovers of plating.

(3) Start-up of the bath rejuvenation system and monitoring the performance of the bath rejuvenation system through 6 metal turnovers of plating.

TECHNICAL BACKGROUND

Electroless nickel (EN) plating, currently being performed at Tinker AFB is an acidic hypophosphite based plating that forms a nickel-phosphorous deposit on the substrate. Traditional acidic

hypophosphite baths consist of nickel sulfate and sodium hypophosphite reagents in an aqueous solution. The reaction by-products from a traditional bath are orthophosphite, sodium, and sulfate ions, which accumulate in the bath. In Stapleton EN bath, the only reagents are nickel and hypophosphite and the only reaction by-product is orthophosphite anion in solution. The orthophosphite anion is removed by treating a slipstream from the bath with calcium hydroxide to precipitate calcium orthophosphite. The calcium orthophosphite precipitate is removed by filtration and the orthophosphite depleted bath solution containing nickel and hypophosphite values is returned to the bath.

In EN plating, bath age is measured in metal turnovers (MTOs). One MTO is defined as when nickel deposit equivalent to the original amount of nickel in the bath has been plated onto the substrate. Traditional EN baths are dumped after 4 MTOs at Tinker AFB due to orthophosphite accumulation. The Stapleton EN bath can theoretically go on plating forever, since the orthophosphite content of the bath is expected to be maintained between 2 and 3 MTOs equivalent. Once the bath has been started, it is allowed to accumulate orthophosphite up to 2 MTOS and the bath rejuvenation is started. Rejuvenation consists of removal of 10 percent of the bath, treatment with calcium hydroxide, filtration and filtrate return. Rejuvenation frequency and time are determined by the plating rate; i.e., if the bath loading and plating rate are such that it requires 40 hours to plate 1 MTO, then the bath rejuvenation is performed once every 4 hours. Bath replenishment of adding nickel and hypophosphite is performed similar to a traditional bath; i.e., nickel concentration level is maintained between 95 percent to 100 percent of full strength.

EN BATH SPECIFICATION, REAGENT AND UTILITY REQUIREMENTS

The tests are to be conducted in a 150-gallon EN plating tank currently in use at Tinker. The bath must be heated and maintained between 191 F and 195 F. The plating bath must be recirculated through a 1 μm cartridge filter at a minimum rate of 20 bath volumes per hour (50 gpm). Air agitation is not desired. The bath should have a pH probe for continuous monitoring of pH.

The utility requirements for the Stapleton EN rejuvenation system are:

Electrical: 110 VAC, 10 Amp

Pneumatic: 85 psi, 60-70 SCFM air

Cooling Water: 10 psig, 15 gpm, 40-80 F

Process Water: 10 psig, 1 gpm, D.I. water preferred.

The plating chemical reagent requirement for the performance test are:

		Cost ($)
Make-Up	150 gal of Enfinity HXIA	1,725
Replenish	400 gal of Enfinity, HXIR	7,800
Control	15 gal of Enfinity, HXIC	268
pH Control	10 gal of Conc. Ammonia	205
Purifier	500 lbs of Calcium Hydroxide	675
TOTAL		$10,673

Battelle requests Tinker AFB's plating shop personnel to ensure that the utility requirements and plating chemical reagent requirements are met prior to the commencement of testing.

The reagent requirement of solution analysis are:

0.1N Iodine Solution	4 lit
0.1N Thiosulfate solution	4 lit
0.59 percent Starch solution	100 mL
6N Hydrochloric Acid	1 lit
Sodium Bicarbonate	250 gm
Acetic Acid (glacial)	I lit

It is expected that these reagents are available in the plating shop chemistry laboratory. Battelle will confirm this with the laboratory; otherwise Battelle will provide these chemicals during the testing period. Battelle will also provide a colorimeter (Hach Company, Model No. DR700) for the nickel concention measurement in the plating bath.

MECHANICAL SHAKEDOWN

Stapleton EN rejuvenation system is a skid mounted, self contained unit that consists of a reactor, filter, a filtrate holding tank and the associated valves and pumps. The schematic representation of the unit showing the major components and solution flow path is shown in Figure C-1. For the purposes of this test plan, the rejuvenation system is taken to be installed. Installation consist of (1) levelling the unit,

(2) connecting the influent line from the EN plating tank: to the units reactor, (3) connecting the filtrate effluent line from the holding tank the EN plating bath, (4) connecting the airline to the air manifold, (5) connecting the process water line to the rinse spray unit, (6) connecting the cooling water lines to the reactor cooling jacket and (7) connecting 110 volt electric supply to the unit.

Mechanical shakedown of the unit consists checking the piping system, valves and pumps for leaks as well as the testing of the system control logic. Mechanical shakedown is performed with hot water. The step-by-step mechanical shakedown testing is detailed below.

(1) A 55 gallon drum is filled with 25 gallons of hot water (130 F or higher) and the reactor influent line is placed inside that drum. The filtrate return line from the rejuvenation unit is placed inside an empty 55 gallon drum. The filtrate holding tank is filled with approximately 20 gallons of cold water.

(2) The ADD button is pushed on the system control panel. The system transfers 15 gallons of hot water from the drum to the reactor and the reactor cooling system is activated. The reactor's agitator is activated. The system also transfers 15 gallons from the filtrate holding tank to the empty drum. In both cases, the volumes of solutions in the drums are measured to make sure that 15 gallons have been transferred from and into the two drums respectively.

(3) The system cools the hot water in the reactor and when the cooling is complete, the READY light comes on the control panel. The temperature of the liquid in the reactor is measured to be close to 100 F or lower.

(4) The TREAT button is then pushed on the front panel and dilute ammonia is manually added to the reactor contents to increase the pH until the ADD PURIFIER light on the panel is turned off. The pH of the contents is then measured and checked to be greater than 8.0.

(5) Once the correct pH has been achieved, the operation of the system is automatic and only the cycle times need to be noted. Once the correct pH is achieved the treatment in the reactor should continue for 2 minutes and the slurry transfer pump to the filter is

activated. The filtrate transfer pump recirculates the filtrate to the reactor for 2 minutes and then transfers the solution to the filtrate holding tank.

(6) The slurry transfer pump is checked to be on for a total of 5 minutes (including recirculation time) and that time should be sufficient for complete transfer of reactor contents to the filter.

(7) The filter vacuum pump is checked to be on once the liquid transfer to the filter is started and vacuum is checked on the gauge to be substantially close to 30 inches of mercury.

(8) Filtrate transfer pump is checked to be on and the transfer of solution to the filtrate holding tank is monitored.

(9) The spray rinse is checked to be activated when the vacuum falls below 20 inches of mercury and the duration of spray rinse is monitored to be close to 8 minutes.

(10) The vacuum pump is checked to shut-off when the vacuum reaches 5 inches of mercury.

(11) The piping, valves, and pumps are checked for leaks during rejuvenation system operations in steps 2 through 10.

(12) Once the filtration is complete and vacuum pump shut-off is monitored, the UNLOAD light is checked to be on and the UNLOAD button is pushed.

(13) The filter unit unload is monitored and RETURN button is pressed to complete the operation.

PLATING BATH START-UP AND MAINTENANCE

Stapleton EN plating bath is made-up by transferring 75 gallons of HXIA solution and 75 gallons of soft or D.I. water to the plating tank. The bath is then heated to 195 F. Bath circulation (through 1 μm cartridge filters) is also turned on while the bath is being heated. Once the bath has reached the

operating temperature of 195, the pH is adjusted to 4.8 using ammonia and the parts and specimens to be plated are immersed in the tank. Specimen razor blades are also immersed in the tank to monitor the plating rate.

The expected plating rate is 0.35 mils/hr. Since the bath nickel concentration needs to be maintained between 95 percent and 100 percent of activity (6.3 grams/lit - 6.6 grams/lit). The frequency of reagent replenishment is dependent on the bath loading. If the bath loading is 0.1 ft^2/gallon, the expected time for 1 MTO of plating is 40 hrs and the bath needs to replenished every two hours. If the bath loading is 0.2 ft^2/gallon, the bath needs to be replenished every hour. Bath replenishment consists of sampling the bath, measuring the nickel content either by EDTA titration or colorimetry and adding the requirement amount of replenisher and control additive. If the nickel concentration is measured at A gm/lit, then the required replenisher (HXIR) addition for a 150 gallons bath is:

$$((6.6 - A) \div 6.6) \times 150 \text{ gallon} \div 4$$

The required control additive (HXIC) amount is

$$((6.6 \div A) \div 6.6) \times 150 \text{ gallon} \div 25$$

For example, if the nickel concentration is measured at 6.3 gm/lit, amount of HXIR to be added is

$$((6.6 - 6.3) \div 6.6) \times 150 \div 4 = 1.7 \text{ gallon}$$

Amount of HXIC to be added is

$$((6.6 \div 6.3) \div 6.6) \times 150 \div 25 = 0.273 \text{ gallon}$$

In addition to replenisher and control additive additions, ammonia is added to the bath to maintain the bath pH between 4.6 and 4.9. Samples of the bath are taken every 8 hours and the bath hypophosphite and orthophosphite concentrations are measured from these samples. The analysis methods to measure the nickel, hypophosphite and orthophosphite concentration are given in Appendix A.

Plating is continued until 2 MTOs equivalent has been plated. At that time, the bath orthophosphite concentration is expected to be approximately 60 gram/lit and the bath is ready for orthophosphite removal (rejuvenation).

TEST OF BATH REJUVENATION SYSTEM

Testing of the Stapleton EN bath rejuvenation system is similar to the system mechanical shakedown except that actual EN solutions is treated instead of water. When the EN bath has plated 2

MTOs equivalent, bath rejuvenation is started. Prior to the start of the rejuvenation, system influent line and filtrate holding tank effluent line are checked to be connected to the EN bath. In addition, a mixture of 7.5 gallons of HXIA (make-up reagent) and 7.5 gallons of water are added to the filtrate holding tank. The bath rejuvenation is detailed below.

(1) The ADD button is pressed on the control panel to initiate rejuvenation. The unit then transfers 15 gallons of EN bath solution to the reactor, transfers 15 gallons of solution from the filtrate holding tank to the EN bath. The unit makes a replenishment addition of HXIR and HXIC equivalent to 10 percent of the bath (3.875 gallon of HXIA and 0.15 gallon of HXIC). It also initiates cooling of the reactor and turns the reactor agitator on. The cooling is stopped when the temperature of the reactor contents reaches 100 F. Then the READY light on the control panel is turned on.

(2) 6.5 Pounds of purifier (calcium hydroxide) is added to the reactor and the TREAT button is pushed to initiate digestion and precipitation of orthophosphite as calcium orthophosphite.

(3) The digestion continues for 2 minutes and then the slurry from the reactor is transferred to the filter. The filter vacuum pump is activated. The filtrate is recirculated back to the reactor for 2 minutes and then transferred to the filtrate holding tank.

(4) The reactor transfer pump transfers all the slurry to the filter (5 minutes) and then shuts off.

(5) Filter vacuum gauge is monitored and the level of vacuum is noted as a function of time.

(6) When the filtration is substantially complete, the vacuum level begins to drop and the spray rinse is activated when the vacuum level falls below 20 inches of mercury. Time for filtration is noted.

(7) Spray rinse of water continues for 8 minutes. The vacuum level will initially rinse and when the filtration of water is complete, the vacuum level will fall. The vacuum pump will shut-off at a vacuum level of 5 inches of mercury. The time of spray rinse filtration

is noted.

(8) After the vacuum filtration is complete, the UNLOAD light will be on and the UNLOAD button is pushed to lifter the filter and dislodge its contents into the collection bin.

(9) The RETURN button will return the filter and the rejuvenation operation is complete.

At the end of rejuvenation, samples of filtrate and filter cake are collected. Filtrate will be analyzed for its nickel, hypophosphite and orthophosphite content by Battelle at Tinker AFB. Filter cake samples will be analyzed solids content by Battelle. The nickel content of the filter cake samples will be analyzed by Battelle at Columbus after the completion of the tests. For the first few rejuvenations, the total weight of the filter cake will also be measured to ensure a closure of the mass balance.

Rejuvenation of 15 gallons of EN bath each time is continued at the rate of 10 such rejuvenations per each MTO. The timing is dictated by the bath loading If the loading is 0.1 ft^2/gallon of solution, then rejuvenation frequency is expected to be once every 4 hours. If the loading is 0.2 ft^2/gallon, the frequency is once every 2 hours.

After the first few rejuvenations, if the orthophosphite concentration increases then the amount of purifier (calcium hydroxide) added each time is increased by half a pound until the orthophosphite level reaches a steady state. In addition, the calcium content of the EN bath will be monitored (using inductively coupled argon plasma) to ensure that it too reaches a steady state once the rejuvenation starts. Due to the presence of calcium, traditional EDTA titration cannot be used to measure the nickel content of the bath and colorimetry technique will be used instead. The colorimeter will be provided by Battelle.

The calcium orthophosphite filter cake collected in the collection bin is the only waste generated in the bath rejuvenation process. It is expected that the solids content of the cake is 40 to 60 percent by weight. The cake also has trace amounts of nickel (1500 to 2500 ppm). The nickel content makes the cake a hazardous waste. The nickel content can be reduced by water washing or acid washing to make the cake nonhazardous. However, no treatment of the cake is planned for the present and it is expected that the filter cake will be disposed as hazardous waste. A 150 gallon EN bath operating at the rate of 50 MTOs per year would produce 2620 pounds (1.31 tons) of filter cake (dry basis) per year. It can be dried in the Tinker AFB plating shop's pretreatment facility to reduce weight and drummed for off-site disposal.

TEST SCHEDULE

The Stapleton EN bath are rejuvenation system is expected to be installed and tested during the month of October 1994. Assuming that 40 hours of plating are necessary for each MTO of plating, the test period is expected to last 6 weeks (i.e., up to 6 MTOs). Battelle and Stapleton personnel expect to be present during the first week (mechanical shakedown and bath start-up), third week (start-up of bath rejuvenation system) and fifth week (conclusion of tests).

TEST SUPPORT REQUIREMENTS

During the performance testing, Battelle requests the participation of one operator (on a full time basis) and one laboratory chemist (on a part-time basis) from Tinker AFB. Although Battelle personnel will perform the start-up, initial plating and rejuvenation tests, the operator is needed as an observer and to coordinate the parts plating, solution transfers and for training purposes. Laboratory chemist is only for short durations to coordinate lab space requirements, reagent supplies and laboratory equipment availability. Battelle also requests the use of lab space in the plating shop laboratory to perform titrations and moisture analysis.

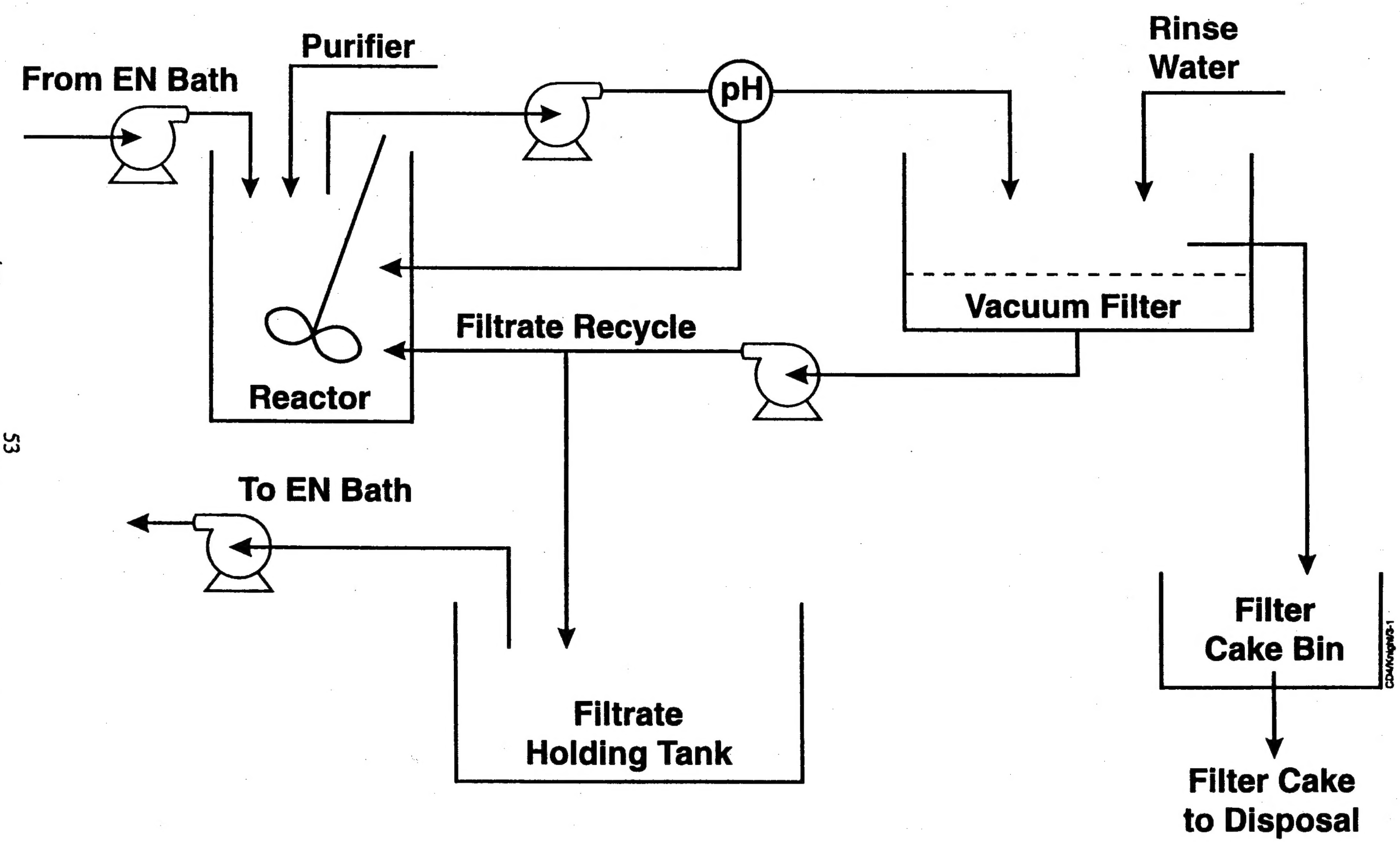

Figure C-1. Process Flowsheet of the Stapleton Electroless Nickel Rejuvenation System.

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